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*List of Physico-chemical Symbols adopted by the Chemical Society.*

[See J.C.S., 1921, 119, 502—512.]

1. *Mathematical Symbols.*

	Usual symbol.	Alternative symbol.
Base of natural (Napierian) logarithms ...	$e$	
Diameter	$d$	
Radius .....	$r$	
Ratio of circumference to diameter	$\pi$	
Summation.....	$\Sigma$	
Variation .....	$\delta$	
Total differential .....	$d$	
Partial differential .....	$\partial$	

2. *Universal Constants.*

Acceleration due to gravity.....	$g$
Mechanical equivalent of heat .....	$J$
Avogadro's constant [number of molecules in 1 gram-molecule (mole)] .....	$N$
Gas constant per mole .....	$R$
Faraday's constant (number of coulombs per gram-equivalent of an ion) .....	$F$
Charge on an electron .....	$e$

3. *General Physics and Chemistry.*

Length .....	$l$	
Height.....	$h$	
Mass .....	$m$	
Time .....	$t$	
Volume .....	$v, V$	
Density (mass per unit volume) .....	$d$	$D$
Pressure .....	$p, P$	
Concentration .....	$c, C$	
Mole fraction .....	$x$	
Critical constants: pressure, volume, tem- perature (centigrade), temperature (absolute), density .....	$\left\{ \begin{array}{l} p_c, v_c \\ t_c, T_c \\ d_c \end{array} \right.$	
Reduced quantities: pressure, volume, temperature, density .....	$\left\{ \begin{array}{l} p_r, v_r \\ t_r, T_r, d \end{array} \right.$	
van der Waals's constants .....	$a, b$	
Fluidity .....	$\phi$	
Viscosity .....	$\eta$	
Surface tension .....	$\gamma$	
Diffusion coefficient .....	$\Delta$	
Atomic weight .....	$A$	
Molecular weight .....	$M$	
Velocity coefficient of reaction .....	$k$	
Equilibrium constant .....	$K, (K_p, K_c)$	
van 't Hoff coefficient .....	$i$	
Degree of dissociation (electrolytic, thermal, etc.) .....		

## 4. Heat and Thermodynamics.

	Usual symbol.	Alternative symbol.
Temperature (centigrade) .....	$t$	
Temperature (absolute) .....	$T$	
Critical temperature .....	$t_c, T_c$	
Reduced temperature .....	$t_r, T_r$	
Critical solution temperature .....	$t_{cs}, T_{cs}$	
Quantity of heat .....	$Q$	
Entropy .....	$S$	
Specific heat .....	$c$	
Specific heat at constant pressure .....	$c_p$	
Specific heat at constant volume .....	$c_v$	
Ratio of specific heats, $c_p : c_v$ .....	$\gamma$	
Molecular heat .....	$O$	
Molecular heat at constant pressure .....	$C_p$	
Molecular heat at constant volume .....	$C_v$	
Latent heat per gram .....	$l$	
Latent heat per mole .....	$L$	
Maximum work (diminution of free energy) .....	$A$	

## 5. Optics.

Wave-length of light .....	$\lambda$	
Refractive index .....	$n$	
Specific refractive power (Gladstone and Dale) .....	$r_g, [r_g]_\lambda^D$	
Specific refractive power (Lorentz and Lorenz) ..	$r_L, [r_L]_\lambda^D$	
Molecular refractive power ..	$R_g, R_L$ $[R_g]_\lambda^D, [R_L]_\lambda^D$	
Angle of optical rotation .....	$[\alpha]$	
Specific rotatory power .....	$M[\alpha]$	
Molecular rotatory power ..	$[\omega]$	
Specific magnetic rotation ..	$M[\omega]$	

## 6. Electricity and Magnetism.

Quantity of electricity ..	$Q$	
Current intensity .....	$I$	
Resistance .....	$R$	$W$
Electromotive force .....	$E$	
Electrode potential, or discharge potential of an ion .....	$E$	$\epsilon$
Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero .....	$E_h, E_c$	$\epsilon_h, \epsilon$
Normal potential, i.e., the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration .....	${}_0E_h, {}_0E_c$	${}_0\epsilon_h, {}_0\epsilon$
Dielectric constant .....	$\epsilon$	
Conductivity (specific conductance) .....	$\kappa$	
Equivalent conductivity .....	$\Lambda$	
Equivalent conductivity at different dilutions—volumes in litres containing 1 gram equivalent .....	$\Lambda_{10}, \Lambda_{20}, \Lambda_{\infty}$	

6. *Electricity and Magnetism*—(continued).

	Usual symbol.	Alternative symbol.
Equivalent conductivity of cation and of anion .....	$\Lambda_k, \Lambda_a$	
Equivalent conductivity of specified ions...	$\Lambda_K, \Lambda_{Cl}$	
Molecular conductivity .....	$\mu$	
Velocity of cation and of anion in cm./sec. when the potential gradient is 1 volt per cm. ....	$U_k, U_a$	
Transport number of kation and of anion ...	$n_k, n_a$	
Magnetic permeability .....	$\mu$	
Magnetic susceptibility .....	$\kappa$	

*List of Symbols, Arranged Alphabetically.*

Symbol.	Name of quantity.
$A$	Atomic weight; maximum work.
$a$	Van der Waals's constant.
$b$	Van der Waals's constant.
$C$	Concentration; molecular heat.
$c$	Concentration; specific heat.
$C_p, C_v$	Molecular heat at constant pressure, and at constant volume.
$c_p, c_v$	Specific heat at constant pressure, and at constant volume.
$D$	Alternative symbol for density.
$d$	Diameter; total differential; density.
$d_c$	Critical density.
$d$	Reduced density.
$E$	Electromotive force; electrode potential.
$e$	Base of Napierian logarithms; charge on an electron.
$E_h, E_c$	Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero.
${}_0E_h, {}_0E_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration.
$F$	Faraday's constant (number of coulombs per gram-equivalent of an ion).
$g$	Acceleration due to gravity.
$h$	Height.
$I$	Current.
$i$	Van 't Hoff's coefficient.
$J$	Mechanical equivalent of heat.
$K$	Equilibrium constant.
$K_e, K_p$	Equilibrium constant, when molar concentrations and partial pressures respectively are employed.
$k$	Velocity coefficient of reaction.
$L$	Latent heat per mole.
$l$	Length; latent heat per gram.
$M$	Molecular weight.
$M[\alpha]$	Molecular rotatory power.
$M[\omega]$	Molecular magnetic rotatory power.
$m$	Mass.
$N$	Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule.
$n$	Refractive index.

*List of Symbols, Arranged Alphabetically—(continued).*

Symbol.	Name of quantity.
$n_+, n_-$	Transport number of cation and of anion.
$n_r$	Refractive index (alternative symbol).
$P$	Pressure.
$p$	Pressure.
$p_c, p_r$	Critical pressure : reduced pressure.
$Q$	Quantity of heat; quantity of electricity.
$R$	Gas constant per mole; electrical resistance.
$R_G, R_L$	Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
$r$	Radius.
$r_G, r_L$	Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
$S$	Entropy.
$T$	Absolute temperature.
$T_c$	Critical temperature (on the absolute scale).
$T_r$	Reduced temperature (absolute).
$T_{c,1}$	Critical solution temperature (absolute).
$t$	Time; temperature (centigrade).
$t_c$	Critical temperature (centigrade).
$t_{c,1}$	Critical solution temperature (centigrade).
$t_r$	Reduced temperature (centigrade).
$U_+, U_-$	Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.
$V$	Volume.
$v$	Volume.
$v_c, v_r$	Critical volume : reduced volume.
$W$	Electrical resistance (alternative symbol).
$w$	Mole fraction.
$\alpha$	Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation.
$[\alpha]$	Specific rotatory power.
$\gamma$	Surface tension; ratio of specific heats.
$\Delta$	Diffusion coefficient.
$\delta$	Variation.
$\partial$	Partial differential.
$\epsilon$	Electrode potential (alternative symbol); dielectric constant.
$\epsilon_h, \epsilon$	Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols).
$\phi, \phi_h, \phi^e$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols).
$\eta$	Viscosity.
$\theta$	Temperature (centigrade), (alternative symbol).
$\kappa$	Specific conductance (conductivity); magnetic susceptibility.
$\Lambda$	Equivalent conductivity.
$\Lambda_{10}, \Lambda_v, \Lambda_\infty$	Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent).
$\Lambda_+, \Lambda_-$	Equivalent conductivity of cation and of anion.
$\lambda$	Wave-length of light.
$\mu$	Molecular conductivity; magnetic permeability.
$\pi$	Ratio of circumference to diameter.
$\Sigma$	Summation.
$\sigma$	Surface tension (alternative symbol).
$\phi$	Fluidity.
$[\omega]$	Specific magnetic rotation.

# JOURNAL

OF

## THE CHEMICAL SOCIETY.

### I.—*Stereoisomerism of Disulphoxides and Related Substances. Part V. The Dioxides of 3:5-Dimethylthiolbenzoic Acid.*

By ERNEST VERE BELL and GEORGE MACDONALD BENNETT.

IN Part III (J., 1928, 3189) a number of pairs of diastereoisomeric disulphoxides of the type  $A\cdot SO\cdot B\cdot SO\cdot A$  were described. Of the two isomerides in such cases, one should be an internally compensated substance, the other externally compensated and potentially optically active. Confirmation of this view was not possible in the examples referred to, owing to the absence of any group in the molecule which would allow of a resolution into the optically active antipodes. The isolation of a suitable pair of disulphoxides is now described, one of which is shown to be separable into enantiomorphous forms.

The substance first studied proved to be unsuitable, for although *s*-diphenylthiolethane-*mm'*-dicarboxylic acid,  $C_2H_4(S\cdot C_6H_4\cdot CO_2H)_2$ , when oxidised in the form of its dimethyl ester, yielded a pair of dioxides, of m. p.  $195^\circ$  and  $126\text{--}129^\circ$  respectively, the hydrolysis of the ester dioxides was accompanied by a disruption of the molecule so that the isomeric free acids were not isolated. This reaction, which has not yet been investigated in detail, is reminiscent of the scission of 1:4-disulphones by alkalis (Stuffer, *Ber.*, 1890, 23, 1408, 3226).

Attention was then directed to 3:5-dimethylthiolbenzoic acid, which was synthesised as follows.

Carboxybenzene-3:5-disulphonyl chloride, the method of preparation of which was improved, was reduced in the usual manner, and the resulting 3:5-dithiolbenzoic acid isolated in the form of its disulphide, 3:5-disulphidobenzoic acid. Methylation of the regenerated dithiol yielded the required dimethylthiolbenzoic acid. The product of oxidation of this acid by hydrogen peroxide was separated by fractional crystallisation into the  $\alpha$ -dioxide, m. p.  $251^\circ$  (decomp.), and the  $\beta$ -dioxide, m. p.  $209^\circ$  (decomp.), which were present in approximately equal proportion.

Considerable difficulty was found in effecting a resolution of either of these isomerides into optically active forms, perhaps on account of the weakness of the acid caused by the presence in the molecule of two sulphoxyl groups of definitely basic properties. The salts of these acids with strychnine, cinchonine, quinine, *l*-menthylamine and the active phenylethylamines could not be obtained crystalline, but those with brucine were suitable for study. The brucine salt of the  $\alpha$ -dioxide was recrystallised unchanged, whereas that of the  $\beta$ -isomeride showed a continuous increase of rotatory power when it was fractionally crystallised from chloroform. Owing to lack of material, the process had to be interrupted after seven crystallisations when it was still evidently incomplete. The acid recovered from the salt of highest rotation was 1-3 : 5-dimethylthiolbenzoic acid dioxide of m. p. 200—202° (decomp.) and had  $[\alpha]_D -99.6^\circ$  for a 1.89% aqueous solution.

From the mother-liquors of the separation an acid was recovered having a positive rotation  $[\alpha]_D +9.1^\circ$  in 2% aqueous solution. When this was fractionally crystallised, the mother-liquors furnished a dextrorotatory acid having  $[\alpha]_D +22.7^\circ$  in 2.64% aqueous solution. The purification could not be carried further with the amount of acid available.

Although the optically active acids were thus not isolated in a state of optical purity, the results afford confirmation of the stereochemical relationship of the pairs of disulphoxides under discussion : the  $\alpha$ -dioxide of dimethylthiolbenzoic acid has the *meso*-configuration, the  $\beta$ -dioxide being potentially active.

#### EXPERIMENTAL.

*s*-Diphenylthiolethane-mm'-dicarboxylic Acid.—*m*-Dithiobenzoic acid (92 g.) was reduced by heating with glucose (92 g.) and sodium hydroxide (48 g. in 100 c.c. of water) in alcohol (300 c.c.) under reflux and addition of a further equal amount of alkali during  $\frac{1}{2}$  hour, followed by ethylene dibromide (65 g.). The solution was cooled and acidified, and the *diphenylthiolethane-mm'-dicarboxylic acid* collected, washed, and dried (yield, 86 g.). It separated from boiling acetic acid as a white micro-crystalline powder, m. p. 265° (decomp.), insoluble in most solvents (Found : C, 57.1; H, 4.45.  $C_{16}H_{14}O_4S_2$  requires C, 57.5; H, 4.2%).

Oxidation of the sodium salt with hydrogen peroxide in aqueous solution yielded a product so sparingly soluble that a pure substance could not be isolated.

The acid (48 g.), dissolved in alkali (17.2 g. of potassium hydroxide in 30 c.c. of water), was added to methyl sulphate (37.6 g.) on the steam-bath. The *dimethyl* ester obtained, after crystallising thrice

from methyl alcohol, formed prisms, m. p.  $73^{\circ}$ , soluble in all the ordinary solvents (Found: C, 59.7; H, 5.0.  $C_{18}H_{18}O_4S_2$  requires C, 59.7; H, 5.0%).

*Isomeric Dioxides of Dimethyl Diphenylthioethanedicarboxylate.*—The ester (25 g.) in glacial acetic acid (500 c.c.) was oxidised with hydrogen peroxide (18.4 g. of 25.9%  $H_2O_2$ ). After 48 hours the solution was evaporated, and the residue fractionally crystallised from 50% acetic acid. The less soluble  $\alpha$ -dioxide was readily obtained pure (yield, 10 g.) and the m. p.,  $195^{\circ}$  (decomp.), was unchanged by further crystallisation (Found: C, 54.2; H, 4.9.  $C_{18}H_{18}O_6S_2$  requires C, 54.8; H, 4.6%).

This substance, reduced with zinc dust and hydrochloric acid in acetic acid, yielded the parent disulphide, m. p.  $73^{\circ}$ , as proved by direct comparison and the m. p. of a mixture.

From the mother-liquors of the above crystallisation a much more soluble  $\beta$ -dioxide was isolated; after being recrystallised several times from methyl alcohol, it melted at  $126$ – $129^{\circ}$  (decomp.). Like the  $\alpha$ -isomeride it yielded the parent disulphide by reduction; there can be little doubt that it is a disulphoxide, but by an oversight the specimen was hydrolysed without having been analysed.

Hydrolysis of these dioxides by alcoholic potassium hydroxide caused some profound disruption of the molecule, the crude acid obtained having an equivalent of 113 (in place of the expected 185).

*Disulphonation of Benzoic Acid.*—By the following modification of Barth and Senhofer's method (*Annalen*, 1871, 159, 217) the use of a sealed tube was avoided and the product isolated as sulphonyl chloride. Benzoic acid (120 g.) was heated in an open flask with fuming sulphuric acid (240 c.c. of 40%  $SO_3$ ) and phosphoric oxide (180 g.) at  $200^{\circ}$  for 1 hour and at  $250^{\circ}$  for 2 hours. The mixture was cooled, chlorosulphonic acid (600 c.c.) added, and the temperature raised to and kept at  $150$ – $180^{\circ}$  for 1 hour so that the chlorosulphonic acid boiled without escaping. The liquid when cool was run slowly into ice-water, and the crude disulphonyl chloride filtered off, washed, and dried (average yield in four preparations, 102 g.).

The carboxybenzene-3:5-disulphonyl chloride crystallised from benzene in stout needles, m. p.  $193^{\circ}$  (Found: Cl, 22.0. Calc.: Cl, 22.3%). Hopegartner (*Monatsh.*, 1893, 14, 690) gives m. p.  $183^{\circ}$ .

*Preparation of 3:5-Dimethylthiolbenzoic Acid.*—Carboxybenzene-disulphonyl chloride (120 g.), dissolved in glacial acetic acid (1800 c.c.) in a 10-litre flask, was reduced by the addition of concentrated hydrochloric acid (280 c.c.) and then, in small portions and with vigorous mechanical stirring, zinc dust (72 g.). When all had dissolved, like amounts of acid and zinc dust were added in a

similar manner. The mixture was allowed to become hot during the process (2—3 hours). The solution was warmed on the steam-bath, and ferric chloride (240 g.) added. Precipitation of the disulphide was hastened by dilution with water and the product was collected, washed, and dried at  $100^{\circ}$  (average yield, 66 g.). 3 : 5-Di-sulphidobenzoic acid was thus obtained as a white powder, m. p.  $195-200^{\circ}$  (decomp.), so sparingly soluble in all available solvents that it could not be crystallised. It has no doubt a much higher molecular weight than that indicated by the formula (Found : S, 33.7.  $C_7H_4O_2S_2$  requires S, 34.8%).

Reduction of this disulphidobenzoic acid (46 g.) was effected by heating with glucose (53 g.) and alcohol (250 c.c.) during the gradual addition of sodium hydroxide (50 g. in 100 c.c. of water). The mixture was then cooled, and methyl sulphate (63 g.) carefully added. After several hours the alcohol was removed in steam and the product precipitated by acidification was collected, washed, and dried at  $100^{\circ}$  (yield, 38 g.). 3 : 5-Dimethylthiolbenzoic acid crystallises from ethyl acetate in square or hexagonal-shaped plates, m. p.  $153^{\circ}$  (Found : S, 29.9; equiv., by titration, 214.  $C_9H_{10}O_2S_2$  requires S, 29.9%; equiv., 214). The sodium salt is very readily soluble in water, but crystallises well from ethyl acetate in clusters of radiating needles, m. p.  $283^{\circ}$  (decomp.) (Found : Na, 9.5.  $C_9H_9O_2S_2Na$  requires Na, 9.7%).

*Oxidation of Dimethylthiolbenzoic Acid to a Pair of Dioxides.*—Hydrogen peroxide (132 g. of 25% strength), diluted with acetic acid (350 c.c.), was gradually added to a solution of dimethylthiolbenzoic acid (104 g.) in acetic acid (2420 c.c.). After 12 hours, the solvent was removed in steam, and the solution evaporated and kept in a vacuum over sodium hydroxide. The crude mixture of dioxides (119 g.) was powdered and extracted with boiling 90% aqueous alcohol (480 c.c.). The residue (39 g.),  $\alpha$ -3 : 5-dimethylthiolbenzoic acid dioxide, was recrystallised from 90% alcohol. The substance crystallises from hot water in long prisms, m. p.  $251^{\circ}$  (decomp.) (Found : S, 26.0; equiv., by titration, 245.6.  $C_9H_{10}O_4S_2$  requires S, 26.0%; equiv., 246.2).

The alcoholic extract of the crude dioxides deposited crystals of  $\beta$ -3 : 5-dimethylthiolbenzoic acid dioxide on cooling, which were purified by several crystallisations from ethyl alcohol (yield, 20 g.). The substance crystallises from water in tufts of fine needles, m. p.  $209^{\circ}$  (decomp.), and is much more soluble in ethyl alcohol and water than the  $\alpha$ -isomeride (Found : S, 25.9%; equiv., by titration, 245.3).

*Examination of the  $\alpha$ - and  $\beta$ -Dioxides as to the Possibility of Resolution into Optically Active Components.*— $\alpha$ -3 : 5-Dimethyl-



thiolbenzoic acid dioxide was dissolved with brucine (1 mol.) in hot chloroform, and the *brucine* salt obtained in large plates containing chloroform of crystallisation. The solvent was removed at 100° in a vacuum; the residual powder had m. p. 170—175° (decomp.) (Found: N, 4.5.  $C_{32}H_{36}O_8N_2S_2$  requires N, 4.4%). The salt, which was very soluble in chloroform, was recrystallised twice from this solvent.

A solution of the ammonium salt of this acid, recovered from the brucine salt by the action of aqueous ammonia and repeatedly extracted with chloroform to remove all the alkaloid, was found to be optically inactive.

The *brucine* salt of  $\beta$ -3 : 5-dimethylthiolbenzoic acid dioxide was prepared in chloroform solution, from which it crystallised in large plates containing solvent of crystallisation. The solvent was lost gradually in air and completely at 100° in a vacuum. The dried salt had m. p. 130° (Found: N, 4.7%) and was readily soluble in chloroform, but sparingly soluble in other solvents. The optical rotatory power in chloroform was  $[\alpha]_D -28.4^\circ$  ( $c = 10.3$ ,  $l = 0.5$ ) and became, after successive crystallisations from this solvent ( $c = 10$ ),  $-28.4^\circ$ ,  $-36.5^\circ$ ,  $-41.5^\circ$ ,  $-46.4^\circ$ ,  $-48.7^\circ$ ,  $-50.0^\circ$ ,  $-52.0^\circ$ ,  $-59.7^\circ$ . At this point the salt had m. p. 184° and was not optically pure, but the quantity of material was not sufficient for further fractionation. The salt (3.5 g.) was decomposed by aqueous ammonia and freed from brucine by repeated extraction of the solution with chloroform. The ammonium salt was converted into the barium salt by means of an excess of barium hydroxide, the ammonia driven off, and carbon dioxide passed in to remove the excess of baryta. The solution was filtered, and the exact equivalent of sulphuric acid (determined on a portion) added. After the barium sulphate had been removed, the solution was evaporated to dryness on the water-bath. The 1-3 : 5-dimethylthiolbenzoic acid dioxide thus obtained (1.4 g.) crystallised from 50% alcohol in minute needles with a straight extinction, m. p. 200—202° (decomp.). It was readily soluble in water or alcohol. Its rotatory power in water was  $[\alpha]_D -99.65^\circ$  ( $c = 1.887$ ,  $l = 2$ ,  $\alpha = -3.76^\circ$ ) (Found: S, 26.0.  $C_9H_{10}O_4S_2$  requires S, 25.9%).

From the chloroform mother-liquors a brucine salt was recovered which had m. p. 140° (decomp.) and a rotatory power of  $[\alpha]_D +0.59^\circ$  in chloroform ( $c = 10$ ,  $l = 0.5$ ).

The salt was freed from brucine and, by the method described above, an optically impure acid (9 g.) was recovered which had  $[\alpha]_D +9.09^\circ$  in water ( $c = 1.980$ ,  $l = 2$ ). When this was recrystallised from ethyl alcohol, the more active portions were found in the mother-liquor, and by fractional crystallisation an optically impure

d-3:5-dimethylthiolbenzoic acid dioxide was obtained, m. p. 190—205° (decomp.), having  $[\alpha]_D + 22.7^\circ$  in water ( $c = 2.640$ ,  $l = 0.5$ ). (Found: S, 25.4%).

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## II.—*Pellitorine, the Pungent Principle of Anacyclus pyrethrum.*

By JOHN MASSON GULLAND and GERALD UERN HOPTON.

WITH one exception, the pungent acid amides of known constitution which occur in nature are alike in containing an aromatic nucleus either in the basic or in the acidic radical. For example, piperine and chavicine (Ott and Eichler, *Ber.*, 1922, 55, 2653; Ott and Lüdemann, *Ber.*, 1924, 57, 214) are piperides of piperic acid and its geometrical isomeride, chavicic acid, respectively, and capsaicin has been shown to be a decenovanillylamide by Nelson (*J. Amer. Chem. Soc.*, 1919, 41, 1115). This characteristic is shared, moreover, by the synthetical pungent amides, which are either derivatives of benzylamine (chiefly vanillylamine) (Nelson, *ibid.*, p. 2121; Ott and Zimmermann, *Annalen*, 1921, 425, 314; Jones and Pyman, *J.*, 1925, 127, 2588) or piperides of arylated (chiefly phenylated) aliphatic acids (Scholtz, *Ber.*, 1895, 28, 1196; Staudinger and Schneider, *Ber.*, 1923, 56, 699; Staudinger and Müller, *ibid.*, p. 711).

The sole exception to these statements is spilanthol, the pungent principle of para cress, *Spilanthus acmella*, Murr. (*S. oleracea*) (Asahina and Asano, *J. Pharm. Soc. Japan*, 1920, 503), whose dihydro-derivative is *n*-decoisobutylamide (*ibid.*, 1922, 85). It is therefore a matter of considerable interest to record the isolation of a purely aliphatic, pungent acid amide, pellitorine, from *Anacyclus pyrethrum*, DC., a plant native to North Africa and gathered chiefly in Algeria. The root of this plant is used medicinally under the names *Pyrethri radix* and pellitory root to stimulate the activity of the salivary glands, and an alcoholic extract was formerly prescribed for the alleviation of bronchitis. The powdered root resembles snuff in appearance, and when chewed causes a persistent tingling sensation and partial insensibility of the tongue, accompanied by profuse salivation (Brit. Pharmacopœia, 1914, p. 322; Squire's "Companion" to the B.P., 1916, p. 1112).

The pungent constituent of pellitory root was first examined by Buchheim (*Arch. exp. Path. Pharm.*, 1876, 5, 455), who isolated a syrup which slowly solidified to a mass of waxy microscopic needles

of very low melting point. He named this material "pyrethrin" and classified it as an amide allied to piperine. By hydrolysis he obtained an oily acid and a base, of which the sulphate was erroneously stated to exhibit all the properties of piperidine sulphate. Later, Dunstan and Garnett (J., 1895, 67, 100) obtained a brown resin which partly crystallised on long standing. They called this product "pellitorine"\* and stated, without advancing any real experimental support, that on hydrolysis it gave rise to what appeared to be a pyridine derivative possessing basic properties. In the following year, Schneegans (*Pharm. Zeit.*, 1896, 41, 668), having used a more laborious process of extraction, recorded the isolation of a somewhat purer specimen of the active principle, which formed colourless needles, m. p. 45°, but no attempt was made to ascertain the constitution of this material.

During the earlier experiments of the present investigation of pellitorine, the method of extraction used by Schneegans was employed, but later it became evident that the simpler procedure of Dunstan and Garnett was equally efficacious when followed by the complex fractional distillation which has been found essential to free the crystalline principle from neutral oily by-products. Earlier workers have commented on the extreme difficulty of eliminating the latter substances. The syrup obtained by evaporating an alcoholic extract of the dried powdered root † was extracted thoroughly with ether, and the ethereal solution was freed from acidic impurities and evaporated. The residual syrup was distilled under highly reduced pressure (0.2—0.5 mm.), and the distillate was subjected to a series of fractionations which are described in detail in the experimental section. Ultimately fractions were obtained which rapidly crystallised in the receiver, and crystallisation of these from light petroleum yielded colourless feathery needles of pure *pellitorine*, m. p. 72°. Considerable quantities remained in the mother-liquor, from which further amounts were obtained by distillation, crystallisation of the solid distillate, and repetition of the process. The yield of pellitorine obtained from 13 kg. of root was 5 g., or 0.04%, but the actual content is probably of the order of 0.06%. Pellitorine is flavourless, but a milligram causes profuse salivation when placed on the tongue. The pungency

\* We propose to retain this name in preference to the earlier "pyrethrin" in order to avoid possible confusion with the constituents of *Pyrethri flores* ("The Extra Pharmacopœia," 1928, 879), the dried flowers of pyrethrum species which are used in powdered form as insecticides (see Staudinger and Ruzicka, *Helv. Chim. Acta*, 1924, 7, 177, and other recent papers).

† The commercial alcoholic extract is very much less satisfactory for experimental purposes than the product freshly obtained in the laboratory.

value was 20 as compared with piperine (100), and was determined by diluting an alcoholic solution until the effect of placing one drop on a cover-glass on the tip of the tongue was just perceptible.

Pellitorine is optically inactive, neutral in character, and unsaturated, since it rapidly decolorises permanganate solution. Elementary analyses and the determination of its molecular weight showed that the formula is  $C_{14}H_{25}ON$ , and the presence of one oxygen atom and one nitrogen atom, and the physiological analogy with piperine, led to the assumption that pellitorine is an acid amide. This view was confirmed by hydrolysis, which took place extremely slowly in boiling alcoholic potash, but was effected more rapidly by heating with dilute hydrochloric acid in a sealed tube. In this way, a crystalline amine hydrochloride, an oily acid, and an oily neutral fraction were obtained.

The neutral fraction contained nitrogen, but as all attempts to crystallise it were unsuccessful and the amount available was small, its further investigation was abandoned.

The basic fraction was shown to be a primary amine by the nitrous acid reaction, and was identified as *isobutylamine* by comparison of the melting points of the hydrochloride, chloroplatinate, and *p-toluenesulphonyl* derivative with those of authentic specimens, by analysis of the first- and last-named derivatives, and by the determination of the melting point of a mixture with authentic *p-toluenesulphonisobutylamide*.

The acid fraction had the characteristic odour of the higher aliphatic acids, was sparingly soluble in water, to which it imparted an acid reaction, and was unsaturated, since it decolorised permanganate solution. In an attempt to purify it by distillation, a small amount of a clear, pale brown oil was collected at 160–200°/0.5 mm., but most of the acid carbonised. This distillate was acidic and unsaturated, but the molecular weight was 271 when determined by titration, a figure considerably higher than that of pellitorine itself. It seemed probable, therefore, that polymerisation or condensation had occurred during the distillation and that the examination of this material would be of little value in arriving at the constitution of pellitorine.

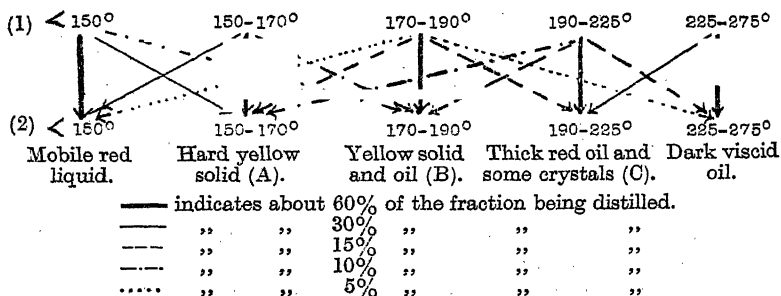
Since the basic portion of the pellitorine molecule is *isobutylamine*, the acidic component must have the formula  $C_9H_{15}\cdot CO_2H$ , and thus lacks four atoms of hydrogen for saturation. Acetylenic linkages being unknown in nature, this deficiency may be accounted for by the presence either of two double bonds or of an alicyclic ring and one double bond, and the choice between these alternatives was made by estimating the amount of hydrogen absorbed during the catalytic reduction of pellitorine. A methyl-alcoholic solution,

when shaken with palladised charcoal in an atmosphere of hydrogen, absorbed the volume corresponding to four atoms of hydrogen, and reduction then ceased completely. The tetrahydropellitorine thus prepared was therefore acyclic, and being a decoisobutylamide, it was subjected to direct comparison, and found to be identical, with a synthetical specimen of *n*-decoisobutylamide. It follows that pellitorine is the isobutylamide of a *n*-nonadienecarboxylic acid, but the position of the double bonds must for the present remain indefinite.

Three observations may be made as the result of this investigation. Firstly, spilanthol and pellitorine are very closely related, differing only in the presence of an extra double bond in the latter, and it is an interesting but not entirely unexpected fact that the plants which yield them are also related, both being members of the order *Compositæ*. Secondly, one double bond at least is necessary for the pungent character of this molecular structure, since *n*-decoisobutylamide is not pungent whereas the two unsaturated compounds are both pungent. *n*-Decoisobutylamide causes no reaction when placed on the tongue, but, after swallowing, a localised tingling sensation lasting for several minutes is felt on the pillars of the fauces. Thirdly, the suggested identity of pellitorine and piperovatine, the pungent principle of *Piper ovatum* (Dunstan and Garnett, J., 1895, 67, 94), is erroneous, since the latter substance has the formula  $C_{16}H_{21}O_2N$  and melts at  $123^{\circ}$ .

#### EXPERIMENTAL.

*Isolation of Pellitorine.*—Powdered pellitory root (13 kg., in batches of 1.5 kg.) was extracted three times with boiling 95% alcohol, and the combined extracts were evaporated to a thin gum, mixed with clean sand, and extracted repeatedly with boiling ether. During this process the mass was stirred as efficiently as possible, but with each extraction the residue became harder, until finally further working became impossible. The ethereal solution, which contained almost all the pellitorine, was shaken twice with dilute sodium carbonate solution, washed with water, dried with sodium sulphate, and evaporated to small volume. The residue, after being transferred to a Claisen flask and freed from ether under diminished pressure, was distilled at the lowest possible pressure attained by a Hyvac pump. During this operation frothing was extremely troublesome. A pale yellow oil was collected at  $150\text{--}275^{\circ}/0.3\text{ mm.}$ ; extensive decomposition then set in, and a hard varnish remained in the flask and was discarded. The distillate was submitted to two fractionations at 0.3 mm. pressure with the following results :



Fraction C was again distilled: 17% was collected at 170—190°/0.3 mm. and solidified (D); the higher fractions were dark-coloured oils. The solid fractions A, B, and D were combined and crystallised repeatedly from light petroleum (b. p. below 40°) by keeping the clear solutions in a refrigerator for some days and washing the deposited crystals with ice-cold solvent. *Pellitorine* forms colourless needles, m. p. 72° (corr.), b. p. 162—165°/0.3 mm., which dissolve very easily in organic solvents but are sparingly soluble in water [Found in material dried at 80°: C, 75.2, 75.0; H, 11.4, 11.3; N, 6.2; *M* in camphor (Rast), 224.  $C_{14}H_{25}ON$  requires C, 75.3; H, 11.2; N, 6.3%; *M*, 223]. It is insoluble in dilute hydrochloric acid and sodium hydroxide solutions, but forms a very faintly yellow solution in concentrated sulphuric acid. Decomposition takes place when a specimen is exposed to the air for some time.

*Hydrolysis of Pellitorine.—Isolation of isobutylamine.* Pellitorine (1 g.) and 2*N*-hydrochloric acid (20 c.c.) were heated in a sealed tube at 150° for 48 hours. There was no increase in pressure in the cooled tube. The products of four experiments were combined and extracted thoroughly with ether (E, see below), and the clear almost colourless acid solution was evaporated to dryness first on the water-bath and then in a desiccator. The residual crystalline isobutylamine hydrochloride (1.8 g.) formed colourless needles, m. p. 174° (Walden, Ulich, and Laun, *Z. physikal. Chem.*, 1925, 114, 290, give m. p. 175.5°), when precipitated from absolute alcoholic solution by means of ether (Found: C, 43.7; H, 11.0. Calc. for  $C_4H_{11}N.HCl$ : C, 43.8; H, 11.0%). The chloroplatinate formed irregular plates, decomp. 217°, when prepared in alcoholic solution.

*p-Toluenesulphonisobutylamide.* isoButylamine hydrochloride (0.24 g.) obtained from pellitorine, recrystallised *p*-toluenesulphonyl chloride (1.3 g.; 3 mols.), ether (25 c.c.), and 2*N*-sodium hydroxide solution (25 c.c.) were shaken mechanically for 12 hours; the smell of the acid chloride could not then be detected. The ethereal layer was separated, washed with water, dried, and freed from solvent. The residual *p*-toluenesulphonisobutylamide crystallised when cold

and separated from light petroleum (b. p. 60—80°) in colourless rhombs, m. p. 75—76° (Found: C, 58.2; H, 7.6.  $C_{11}H_{17}O_2NS$  requires C, 58.2; H, 7.5%). A specimen prepared in a similar manner from authentic *isobutylamine* formed colourless rhombs, m. p. 75—76° alone or when mixed with the material prepared from *pellitorine*.

*Examination of the ethereal extract E* (see above). The ethereal solution was shaken repeatedly with sodium carbonate solution to remove the acidic contents, and was then washed with water, dried, and evaporated. The neutral oily residue (1.6 g.) distilled at 160—190°/0.5 mm.; the clear distillate, which had an odour not unlike that of peaches, contained nitrogen and did not crystallise when kept in a refrigerator for some days. It was not examined further.

The acidic fraction (1.8 g.), which was liberated as a dark oil from the carbonate solution, was perceptibly purified neither by treatment with charcoal nor by repeated precipitation from alkaline solution, and an attempt was made to distil it. Much carbonisation took place, and the distillate (0.5 g.; b. p. 160—200°/0.5 mm.; mol. wt. 271) failed to crystallise. The acid chloride, prepared by means of phosphorus pentachloride in chloroform solution, yielded an oily anilide and an amide; the latter crystallised from very dilute methyl alcohol in colourless plates, m. p. 35°, which dissolved very readily in organic solvents.

*Tetrahydropellitorine* (*n-Decoisobutylamide*).—A solution of *pellitorine* (0.342 g.) in methyl alcohol (25 c.c.) was run into a suspension of palladised charcoal (from palladous chloride, 0.2 g., and charcoal, 1.5 g.) in methyl alcohol (25 c.c.) which was stirred mechanically in an atmosphere of hydrogen: the absorption of hydrogen (69.6 c.c., corrected to N.T.P.) ceased completely after 3 minutes. The volume of hydrogen required for the addition of 4 atoms of hydrogen to  $C_{14}H_{25}ON$  is 68.2 c.c. The solution was filtered from charcoal, the methyl alcohol distilled, and the residual oil dissolved in ether and dried. Removal of the solvent yielded tetrahydropellitorine as a colourless oil which rapidly crystallised in flat needles, m. p. 35° (corr.), very soluble in organic solvents (Found: C, 74.1; H, 12.7. Calc. for  $C_{14}H_{29}ON$ : C, 74.0; H, 12.8%). This material melted at 36° when mixed with synthetic *n-decoisobutylamide*, m. p. 36°; the necessary decoic acid, m. p. 31°, was obtained by the hydrolysis of a carefully fractionated sample of commercial ethyl decoate, and the amide was obtained by the action of *isobutylamine* on the acid chloride in benzene solution.

## III.—1:3-Dithiolan.

By DAVID T. GIBSON.

THE isolation of 1:3-dithiolan,  $\begin{matrix} \text{CH}_2\cdot\text{S} \\ \text{CH}_2\cdot\text{S} \end{matrix} > \text{CH}_2$ , and of 1:3-dithian, although inferred (Baumann and Walter, *Ber.*, 1893, **26**, 1129; Autenrieth and Wolff, *Ber.*, 1899, **32**, 1375), has not been described. The preparation of ethylene dimercaptan (Meyer, *Ber.*, 1886, **19**, 3263; Fasbender, *Ber.*, 1887, **20**, 461; Frasseti, *Ber.*, 1905, **38**, 491) may be more conveniently effected by an extension of Purgotti's method (*Gazzetta*, 1892, **22**, 416). The condensation of formaldehyde and ethylene dimercaptan actually yields two products, dithiolan and a voluminous solid *polymeride*. Dithiolan could not be obtained by the reduction of ethylene trithiocarbonate (compare Hurtley and Smiles, J., 1926, 1821), but it is directly obtained by distilling a mixture of formaldehyde, sodium ethylene thiosulphate, and hydrochloric acid.

Dithiolan is converted by hydrogen peroxide into a liquid *monoxide*, the green solution of which in sulphuric acid immediately becomes deep red on addition of a drop of anisole. With platinic chloride the monoxide gives an orange-red *compound*,  $(\text{C}_2\text{H}_5\text{S}_2)_2\text{PtCl}_3\cdot\text{H}_2\text{O}$  (compare Tschugaev and Benewolenski, *Z. anorg. Chem.*, 1913, **82**, 420). In presence of hydrochloric acid, one molecule of the monoxide undergoes oxidation at the expense of another, one-half of the material being recovered as dithiolan, and the remainder precipitated as an insoluble amorphous *dioxide* (compare the first oxidation product of tetramethoxythianthren; Fries, Koch, and Stunkenbrock, *Annalen*, 1929, **468**, 166).

1:3-Dithian was obtained by treating trimethylene dibromide with sodium thiosulphate, formaldehyde, and hydrochloric acid.

## EXPERIMENTAL.

*Ethylene Dimercaptan*.—Ethylene dibromide (200 c.c.), water (20 c.c.), sodium thiosulphate (100 g.), and alcohol (100 c.c.) were mechanically shaken for 6 hours at 50–60°. The stiff pasty product was collected, boiled with excess of hydrochloric acid, and distilled in steam, yielding 9 g. of the mercaptan, b. p. 144°. If the hydrolysis is conducted with alkali, no mercaptan is formed.

*Condensation of Ethylene Dimercaptan with Formaldehyde*.—The mercaptan was slowly added to formalin solution, containing a trace of hydrochloric acid, below 25°. The clear solution, when gently warmed, suddenly became turbid with separation of 1:3-dithiolan and its *polymeride*. The former was distilled in steam and purified as described below. The *polymeride*, m. p. 105–110°, after, being



washed with ether, was practically insoluble in any organic solvent; it dissolved with effervescence in nitric acid, giving a red solution [Found : C, 34.1; H, 6.1.  $(C_3H_6S_2)_n$  requires C, 34.0; H, 5.7%].

1 : 3-Dithiolan was more conveniently obtained by treating sodium ethylene thiosulphate, prepared as described above, with a mixture of hydrochloric acid and twice the calculated amount of formalin. Steam distillation furnished a 50–60% yield of the dithiolan, which was purified by refluxing it for several hours with aqueous alkali; it then boiled at  $175^\circ/760$  mm. and  $61^\circ/11$  mm. and had  $d^{20}_D$  1.259,  $n^{15}_D$  1.5975, whence  $[R_L]_D = 29.7$  (calc., 29.8) (compare Le Bas, *Trans. Faraday Soc.*, 1920, **15**, 231) (Found : C, 34.2; H, 5.8;  $M$ , 111.  $C_3H_6S_2$  requires C, 34.0; H, 5.7%;  $M$ , 106). It yielded a mercurichloride, m. p.  $119^\circ$ , on treatment with mercuric chloride, and gave Baumann and Walter's disulphone (*loc. cit.*), m. p.  $224^\circ$ , in 80% yield on oxidation with perhydrol in glacial acetic acid at  $50^\circ$ .

1 : 3-Dithiolan Monoxide.—Perhydrol (9 c.c.) in 20 c.c. of glacial acetic acid was added very slowly to specially purified 1 : 3-dithiolan (10 c.c.) in 20 c.c. of glacial acetic acid. After several days, the solvent was removed below  $40^\circ$ , first at 11 mm. and finally at 1 mm. (neglect to remove every trace of solvent at as low a temperature as possible causes complete decomposition in the subsequent distillation) and the residue was distilled over a trace of magnesium carbonate, giving 8 g. of an oil, b. p.  $115$ – $120^\circ/1$  mm. (Found : C, 30.1; H, 5.3;  $M$ , 118.  $C_3H_6OS_2$  requires C, 29.5; H, 5.0%;  $M$ , 122).

The monoxide is miscible with water, and is decomposed by warm hydrochloric acid into dithiolan (identified by its mercurichloride, m. p.  $119^\circ$ ) and a dioxide; m. p.  $134^\circ$  (Found : C, 26.3, 26.4; H, 4.7, 4.3.  $C_3H_6O_2S_2$  requires C, 26.0; H, 4.4%). It is insoluble in all the usual solvents, including aqueous alkali.

With platinic chloride, an aqueous solution of dithiolan monoxide yields a flocculent precipitate, which may be recrystallised from hot water; m. p.  $146$ – $150^\circ$  (decomp.) [Found : C, 14.0; H, 2.7; Cl, 20.3; Pt, 36.7.  $(C_3H_5S_2)_2PtCl_3 \cdot H_2O$  requires C, 13.6; H, 2.3; Cl, 20.1; Pt, 36.8%].

With methyl iodide, dithiolan monoxide yields a *methiodide*, m. p.  $96^\circ$  (Found : I, 47.7.  $C_4H_9OIS_2$  requires I, 48.1%).

1 : 3-Dithian.—Trimethylene dibromide (30 c.c.), sodium thiosulphate (120 g.), and alcohol (100 c.c.) were shaken at  $60^\circ$  for 2 days. The solid which separated was distilled in steam with formalin and hydrochloric acid, and the distillate extracted with ether. The dithian crystallised readily and melted at  $54^\circ$  (Found : C, 40.1, 40.0; H, 7.1, 6.6.  $C_4H_8S_2$  requires C, 40.0; H, 6.7%). On oxid-

ation with perhydrol in glacial acetic acid, it gave Autenrieth and Wolf's disulphone (*loc. cit.*), m. p. 330°, in almost quantitative yield.

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UNIVERSITY OF GLASGOW.

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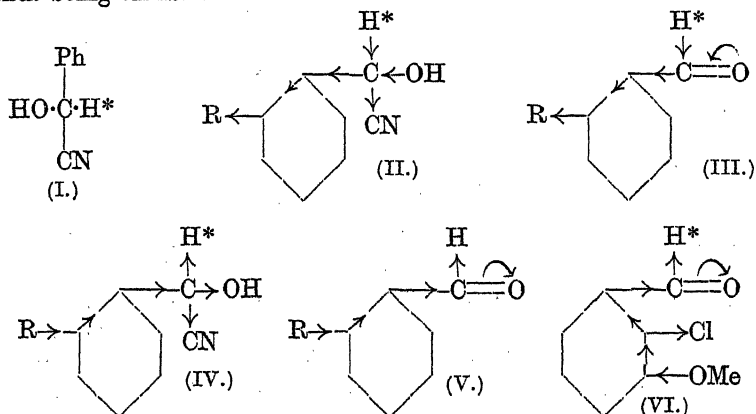
#### IV.—*The Influence of Substituents on the Benzoin Reaction.*

By HERBERT HENRY HODGSON and WOLF ROSENBERG.

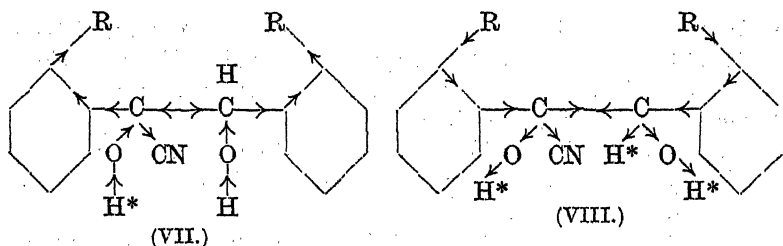
THE present investigation in conjunction with the results of Ekecrantz and Ahlqvist (*Arkiv Kemi Min. Geol.*, 1908, 3, No. 13) shows that substituents inhibit the benzoin reaction in varying degrees according to their electronic character. On Lapworth's theory (J., 1903, 84, 1004) that the possibility of the benzoin condensation depends on the mobility of the hydrogen atom \* in the initially formed mandelonitrile (I), (a) a *meta*-directing group (R) will activate this hydrogen \* (II) but deactivate the carbonyl group of the second molecule of the reacting benzaldehyde (III), and (b) when R is *op*-directing, H\* (IV) is deactivated but CO (V) is activated. In case (a) the benzoin condensation of (II) and (III) would appear to depend on the relative activation and deactivation: *e.g.*, when R is NO<sub>2</sub> (strong), it over-activates H\* but renders the CO (III) much less capable of forming the initial cyanohydrin, hence excessive production of nitrobenzoic acid occurs (compare Lapworth and Manske, J., 1928, 2533); when R is Cl (weak), only 5% of *o*-chlorobenzoic acid can be isolated, and benzoin formation ensues. In case (b), although cyanohydrin formation may readily occur, the subsequent benzoin condensation of (IV) and (V) may be inhibited because of the deactivated hydrogen \*: *e.g.*, (1) attempts to produce a benzoin from any monohydroxybenzaldehyde have all failed owing to the presence of anionoid oxygen ( $R = \overset{\ominus}{O}$ ), and (2) although the alkyloxybenzaldehydes all give benzoin, the introduction of a second group as in *p*-benzyloxy-*m*-methoxybenzaldehyde brings about the necessary deactivation and no benzoin is formed.

On the above theory, 2-chloro-3-methoxybenzaldehyde produces a benzoin more readily than does 3-methoxybenzaldehyde owing to a reduction by chlorine of the hydrogen deactivation produced by the methoxyl group (VI). 3-Chloro-2-hydroxybenzaldehyde (80%) and 3-chloro-4-hydroxybenzaldehyde (25%), however, appear to

react only as far as the cyanohydrin stage, and Ekecrantz and Ahlqvist (*loc. cit.*) found that *p*-hydroxybenzaldehyde and vanillin were unreactive towards alcoholic potassium cyanide, the complete internal satisfaction of the electronic demands of the carbonyl group thus being exhibited.



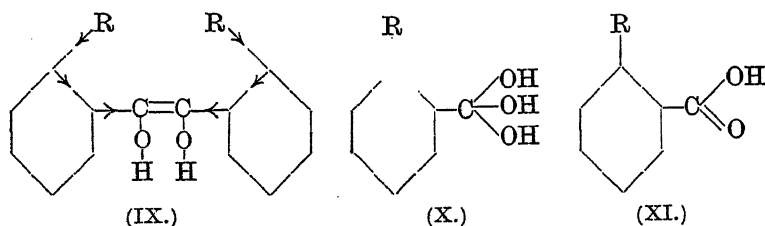
The possibility of the benzooin reaction taking place might also be considered from the standpoint of the influence of groups on the stabilities of the respective hypothetical intermediate benzoin cyanohydrins (VII and VIII) (Lapworth, *loc. cit.*):



(a) When  $\text{R}$  is *meta*-directing (VII), the  $\text{H}^*$  tends to be ionised, formation of hydrogen cyanide thereby being promoted, so that, when  $\text{R}$  is sufficiently strong (*e.g.*,  $\text{NO}_2$ ), the initial formation of mandelonitrile is prevented and no benzooin reaction can occur.

(b) When  $\text{R}$  is *op*-directing (VIII), the hydrogens  $^*$  are deactivated and  $\text{CN}$  is activated. Subsequent reaction can and, so far as the end-products are evidence, does occur in two ways: (1) the formation of a benzooin, and (2) the intermediate formation of the isomeride (IX) of this benzooin, which is hydrolysed, giving a benzyl alcohol and an unstable phenylorthoformic acid (X), the latter changing to a stable benzoic acid (XI); *e.g.*, from *o*- and *p*-anisaldehydes, con-

siderable quantities of *o*- and *p*-anisic acids are produced together with the *o*- and *p*-anisoin.



### EXPERIMENTAL.

**2 : 2'-Dichlorobenzoin.**—Solutions of *o*-chlorobenzaldehyde (5 g.) in alcohol (10 c.c.) and of potassium cyanide (1 g.) in water (4 c.c.) were heated together under reflux on the water-bath for 1 hour and poured into aqueous sodium bicarbonate, which dissolved the *o*-chlorobenzoic acid formed (5%); after 1 hour, the whole was extracted with ether, and the extract shaken with aqueous sodium bisulphite to remove unchanged *o*-chlorobenzaldehyde. (Benzoin and benzils do not easily form hydrazones or sodium bisulphite addition compounds, a fact which has been utilised for the removal of unchanged initial material in the various reactions studied.) The 2 : 2'-dichlorobenzoin (40% yield) was obtained by removal of the ether and extraction of the residue with acetic acid or alcohol, from which it separated in white prisms, m. p. 56—57° (Found : Cl, 25.0.  $C_{14}H_{10}O_2Cl_2$  requires Cl, 25.2%). The final resinous residue (40%) contained nitrogen, presumably as cyanohydrin, but no alcohol corresponding to *o*-chlorobenzoic acid was isolated (compare Ekecrantz and Ahlqvist, *loc. cit.*). The acid may have been formed partly by air oxidation, since the amount increased when the reaction mixture was kept for several days.

An alcoholic solution of 2 : 2'-dichlorobenzoin when treated with aqueous-alcoholic sodium hydroxide gives a brownish-red colour, deeper than that given by unsubstituted benzoin, which deepens on boiling but disappears on shaking (compare Hantzsch and Glover, *Ber.*, 1907, 40, 1520), returns on keeping but disappears again on shaking, and so on.

2 : 2'-Dichlorobenzil was prepared by the usual nitric acid method, but better results were obtained when 2 : 2'-dichlorobenzoin (1 g.), dissolved in glacial acetic acid (10 c.c.), was heated with a slight excess of chromium trioxide on the water-bath for 1 hour. After dilution with water and extraction with ether, the benzil crystallised from benzene in pale yellowish-green prisms, m. p. 128° (Found :

Cl, 25.2.  $C_{14}H_8O_2Cl_2$  requires Cl, 25.4%), which were sparingly soluble in boiling alcohol, ether, and glacial acetic acid.

3 : 3'-*Dimethoxybenzoin* (*m-Anisoin*).—Powdered potassium cyanide (1 g.) was added to a boiling solution of *m*-methoxybenzaldehyde (10 g.) in 50% aqueous alcohol (30 g.). After boiling for 2 hours, the mixture was kept over-night in a freezing mixture, and the oily yellowish-brown solid obtained was removed, freed from oil, and washed with ether; the residue crystallised from alcohol in micro-prisms (2 g.), m. p. 41–42° (Found: C, 70.8; H, 5.7.  $C_{16}H_{16}O_4$  requires C, 70.6; H, 5.9%).

2 : 2'-*Dichloro-3 : 3'-dimethoxybenzoin*, readily obtained by the ordinary method, crystallised from alcohol in prisms, m. p. 133–134° (Found: Cl, 20.6.  $C_{16}H_{14}O_4Cl_2$  requires Cl, 20.8%). The *p*-nitrophenylhydrazone crystallised from glacial acetic acid in yellow needles, m. p. 129° (Found: N, 9.0; Cl, 14.8.  $C_{22}H_{19}O_5N_3Cl_2$  requires N, 8.8; Cl, 14.9%), which gave a reddish-violet colour with aqueous-alcoholic sodium hydroxide.

2 : 2'-*Dichloro-3 : 3'-dimethoxybenzil*, prepared in the same way as 2 : 2'-dichlorobenzil, crystallised from benzene in very pale greenish-yellow prisms, m. p. 200° (Found: Cl, 20.8.  $C_{16}H_{12}O_4Cl_2$  requires Cl, 20.9%).

2 : 2'-*Dichloro-3 : 3'-dimethoxybenzilic acid*, formed by boiling 2 : 2'-dichloro-3 : 3'-dimethoxybenzil (5.5 g.), dissolved in alcohol (11 g.), with a mixture of potassium hydroxide (5.5 g.) and water (11 g.) for 10 minutes, crystallised from water in colourless needles, decomp. 182–185° (Found: Cl, 20.0.  $C_{16}H_{14}O_5Cl_2$  requires Cl, 19.9%).

2-*Chloro-3-methoxybenzoic acid* was prepared by gradually adding a saturated aqueous solution of potassium permanganate to a boiling aqueous suspension of 2-chloro-3-methoxybenzaldehyde until it was no longer decolorised and the aldehydic odour had disappeared. The excess of permanganate was destroyed by sulphur dioxide; the solution on cooling deposited colourless needles, m. p. 161.5° after recrystallisation from water (Found: Cl, 19.1.  $C_8H_7O_3Cl$  requires Cl, 19.0%).

*Approximate Determination of the Reactivities of Various Aldehydes from the Quantities of Resinous Products formed.*—These experiments were undertaken to investigate the combined influence of two groups of opposed electronic effects. In each case the benzoïn reaction mixture was poured into water and acidified with acetic acid, the precipitate dissolved in ether, and the solution washed with aqueous sodium bisulphite to remove unchanged initial material, and dried; the ether was then removed, and the residue weighed.

Benzaldehyde.	Unchanged material (g.).	Reaction product (g.).
3-Hydroxy- .....	4.0	9.5
3-Chloro-2-hydroxy- .....	0.4	2.9
3-Chloro-4-hydroxy- .....	4.5	1.5

From the resinous products, and from the corresponding synthetic cyanohydrins, nothing could be obtained crystalline.

The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals.

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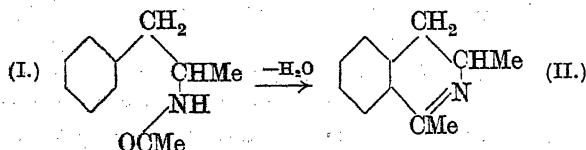
[Received, October 4th, 1929.]

## V.—dl- $\beta$ -Phenylisopropylamine and Related Compounds.

By DONALD HOLROYDE HEY.

$\beta$ -PHENYLISOPROPYLAMINE has been obtained by Edeleano (*Ber.*, 1887, 20, 618) by the action of bromine and aqueous potash on phenylisobutyramide and its chloroplatinate also is described. The hydrochloride of the *d*-form was obtained by Jones and Wallis (*J. Amer. Chem. Soc.*, 1926, 48, 180) by the hydrolysis of *d*- $\alpha$ -benzylethylcarbimide with concentrated hydrochloric acid. In the present investigation the racemic base was readily obtained by the reduction of *benzyl methyl ketoxime* by means of sodium amalgam in dilute acetic acid solution. Benzyl methyl ketoxime, previously described as a thick oil by Dollfus (*Ber.*, 1892, 25, 1918; 1893, 26, 1971), has now been obtained in a pure crystalline form, melting at 70°.

The *acetyl* derivative (I) of the base, on treatment with phosphoric oxide in boiling toluene (compare Pictet and Kay, *Ber.*, 1909, 42, 1973), gave 1 : 3-dimethyl-3 : 4-dihydroisoquinoline (II), which was isolated in the form of its *picrate*.



The reduction of *isonitrosopropiophenone* under various conditions gives rise to a variety of products, generally in poor yield (Gudeman, *Ber.*, 1889, 22, 562; Behr-Bregowski, *Ber.*, 1897, 30, 1521; Gabriel, *Ber.*, 1908, 41, 1127; Rabe, *Ber.*, 1912, 45, 2166; Calliess, *Arch. Pharm.*, 1912, 250, 141), but the only instance of its direct

reduction to *dl*- $\beta$ -hydroxy- $\beta$ -phenylisopropylamine (norephedrine),  $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{NH}_2$  (compare the reduction of benzil monoxime to  $\beta$ -hydroxy- $\alpha\beta$ -diphenylethylamine; Polonowska, *Ber.*, 1888, **21**, 488), has been reported by Rabe, who obtained the base in small yield by using colloidal palladium. Since the inception of this work, however, Hartung and Munch (*J. Amer. Chem. Soc.*, 1929, **51**, 2262) have obtained  $\beta$ -hydroxy- $\beta$ -phenylisopropylamine (phenylpropanolamine) in good yield from isonitrosopropiophenone by catalytic reduction with palladised charcoal. In the present investigation, although a number of reducing agents were employed under various conditions, the desired result was not effected, since the isonitrosopropiophenone exhibited a very marked stability [compare the relatively facile reduction of benzyl methyl ketoxime (see experimental part) and of propiophenone oxime (Billon, *Compt. rend.*, 1926, **182**, 470)], and much of it was recovered unchanged. The great stability of this oximino-ketone has been the subject of comment by Coles, Manske, and Johnson (*J. Amer. Chem. Soc.*, 1929, **51**, 2269).

Melting points of isonitrosopropiophenone varying from  $108^\circ$  to  $115^\circ$  are recorded in Beilstein's "Handbuch der organischen Chemie." The specimen prepared by Hartung and Munch (*loc. cit.*) and crystallised from toluene, melted at  $106\text{--}106.5^\circ$ , whereas the preparation used in this investigation was crystallised from water, melted at  $114.5^\circ$ , and gave rise to metallic complex formation with iron, cobalt, and copper (compare  $\alpha$ - and  $\beta$ -benzil monoximes, Tschugaev, *Z. anorg. Chem.*, 1905, **46**, 148; Taylor and Ewbank, *J.*, 1926, 2818; Pfeiffer and Richarz, *Ber.*, 1928, **61**, 103).

#### EXPERIMENTAL.

*Benzyl Methyl Ketoxime.*—Solutions of 18 g. of benzyl methyl ketone in 40 c.c. of alcohol and of 10 g. of hydroxylamine hydrochloride in 20 c.c. of water were mixed and, after addition of 6 g. of sodium hydroxide in the minimum quantity of water, heated on a boiling water-bath for  $1\frac{1}{2}$ —2 hours. The solution was then diluted considerably, acidified, and extracted with ether. After being washed with a concentrated solution of calcium chloride and dried, the ether was evaporated; the residual thick red oil, which solidified, after several recrystallisations from light petroleum (b. p.  $60\text{--}80^\circ$ ), gave the *oxime* in white prismatic crystals, m. p.  $70^\circ$  (Found: C, 72.8; H, 7.4; N, 9.5.  $\text{C}_9\text{H}_{11}\text{ON}$  requires C, 72.5; H, 7.4; N, 9.4%).

*Reduction of Benzyl Methyl Ketoxime.*—To a well-stirred solution of 10 g. of benzyl methyl ketoxime in glacial acetic acid, diluted with water, 300 g. of 3% sodium amalgam were gradually added. After 6 hours the solution was made alkaline and extracted with ether and the base was extracted from the ethereal solution with

dilute hydrochloric acid; or alternatively the alkaline solution was steam-distilled, the base being collected in dilute hydrochloric acid. The free base, liberated by the addition of alkali, was extracted with ether and dried over solid caustic potash. Evaporation of the ether left a yellowish oil with an ammoniacal odour, which on distillation gave pure *dl*- $\beta$ -phenylisopropylamine as a colourless oil, b. p.  $205^{\circ}$  (Edeleano, *loc. cit.*, recorded  $203^{\circ}$ ). The base readily combines with carbon dioxide.

The *acetyl* derivative, formed in the usual manner, crystallised from aqueous alcohol in fine white needles. These melted initially at  $64^{\circ}$ , but at  $93^{\circ}$  after being kept for some time in a vacuum (Found: C, 74.7; H, 8.6; N, 8.1.  $C_{11}H_{15}ON$  requires C, 74.6; H, 8.5; N, 7.9%).

The *picrate*, prepared from picric acid and the base in concentrated solution and recrystallised from alcohol, gave yellow transparent prisms, containing one molecule of alcohol, which melted at  $143^{\circ}$  (Found: C, 49.9; H, 5.5; N, 13.8.  $C_{15}H_{16}O_7N_4 \cdot C_2H_5 \cdot OH$  requires C, 49.8; H, 5.4; N, 13.7%).

The *hydrochloride*, prepared from hydrogen chloride and the base in dry ether, was rapidly collected, washed with pure dry ether, and transferred to a desiccator evacuated over solid caustic potash. It is extremely hygroscopic and melts at  $145$ – $147^{\circ}$  (Found: C, 63.3; H, 8.6; N, 8.1; Cl, 20.8.  $C_9H_{13}N \cdot HCl$  requires C, 63.0; H, 8.2; N, 8.2; Cl, 20.7%).

*Action of Phosphoric Oxide on Aceto-dl- $\beta$ -phenylisopropylamide.*—A solution of 2 g. of the acetyl compound in toluene was boiled for 3 hours with 4 g. of phosphoric oxide (compare Pictet and Kay, *loc. cit.*). The solution was then made alkaline, the base extracted with ether, the toluene and ether evaporated, and the small residue of oil converted into picrate in concentrated alcoholic solution. Recrystallisation from alcohol gave 1:3-*dimethyl*-3:4-*dihydroisoquinoline picrate* in yellow fern-like crystals, m. p.  $136^{\circ}$  (Found: C, 52.9; H, 4.4; N, 14.35.  $C_{17}H_{16}O_7N_4$  requires C, 52.6; H, 4.1; N, 14.4%).

*isoNitrosopropiophenone.*—This was prepared from propiophenone and amyl nitrite by Claisen and Manasse's method (*Ber.*, 1889, 22, 529); it crystallised from water in fine needles, m. p.  $114.5^{\circ}$ .

*Complex formation.* (a) *With iron.* When aqueous ferrous sulphate solution was shaken with *isonitrosopropiophenone* and dilute caustic soda solution added, a blue colour was produced which, on shaking with benzene, passed into this solvent.

(b) *With cobalt.* To a solution of 3 g. of *isonitrosopropiophenone* in very dilute alcohol was added an aqueous solution containing 4.5 g. of cobalt acetate. A dense yellowish-brown precipitate



formed almost immediately, which was collected after a while and washed with water, dilute alcohol, and finally with a little ether [Found : Co, 10.9; C, 59.9; H, 4.5; N, 7.8.  $\text{Co}(\text{C}_9\text{H}_8\text{O}_2\text{N})_3$  requires Co, 10.8; C, 59.45; H, 4.4; N, 7.7%].

(c) *With copper*. In a similar way, from 3 g. of copper acetate and 2 g. of isonitrosopropiophenone, a dense dark bluish-green precipitate was obtained, which was washed with water, dilute alcohol, and ether [Found : Cu, 25.9; C, 44.7; H, 3.8; N, 5.75.  $\text{CuOH}(\text{C}_9\text{H}_8\text{O}_2\text{N})$  requires Cu, 26.2; C, 44.5; H, 3.7; N, 5.8%].

The author desires to thank Dr. F. Challenger for his advice and interest in this work.

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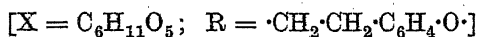
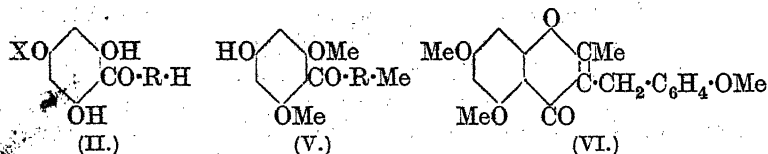
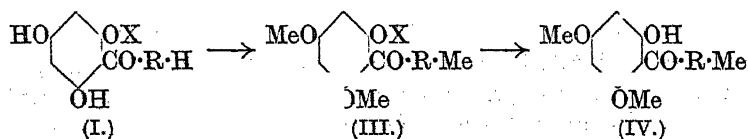
## VI.—*Natural Glucosides. Part I. The Constitution of Phloridzin.*

By FRANCIS RABAN JOHNSON and ALEXANDER ROBERTSON.

THE glucoside phloridzin, which occurs in the bark of apple, pear, plum, and cherry trees, was first isolated in 1835 by De Koninck (*Annalen*, **15**, 75, 258) from the root bark of the apple tree, and was correctly analysed by Stas (*Ann. Chim. Phys.*, 1836, **61**, 367), who found that it was decomposed by mineral acids into phloretin and a sugar which he believed to be glucose. The glucoside was subsequently examined by a number of workers and the empirical formula  $\text{C}_{21}\text{H}_{24}\text{O}_{10} \cdot 2\text{H}_2\text{O}$  was established by Rennie (*J.*, 1887, **51**, 634), who effected the hydrolysis by dilute sulphuric acid with the production of phloretin,  $\text{C}_{15}\text{H}_{14}\text{O}_5$ , and glucose. The latter result was confirmed independently by Fischer (*Ber.*, 1888, **21**, 988) and by Schunck and Marchlewski (*Ber.*, 1893, **26**, 942; *Annalen*, 1894, **278**, 349). A synthesis of phloretin by Fischer and Nouri (*Ber.*, 1917, **50**, 611) definitely established its constitution (compare Zemplén and co-workers, *Ber.*, 1928, **61**, 2486; Rosenmund and Rosenmund, *ibid.*, p. 2608). That the glucose residue of phloridzin is attached to the phloroglucinol nucleus was shown by Cremer and Seuffert (*Ber.*, 1912, **45**, 2565), who, by the action of warm baryta water, obtained phloretic acid and phlorin, phloroglucinol  $\beta$ -glucoside. This glucoside had previously been synthesised by Fischer and Strauss (*Ber.*, 1912, **45**, 2467).

As the result of previous work, phloridzin may be represented by formula (I) or (II), and therefore should, on methylation of the phenolic hydroxyl groups and hydrolysis of the product, give a trimethylphloretin (IV or V). The glucoside was methylated in

acetone solution by means of methyl iodide and anhydrous potassium carbonate, a method which has been shown by Robinson (J., 1928, 1457) to effect the methylation of *O*-benzoylphloroglucinaldehyde. In order to ensure complete alkylation of the phenolic groups, prolonged treatment with an excess of the methylating agents was essential. The product, which gave no evidence of the presence of an unprotected phenolic hydroxyl group, appeared to be partly methylated in the sugar residue and could not be purified. Hydrolysis of the crude material, however, with aqueous methyl-alcoholic sulphuric acid gave 6-hydroxy-2:4:4'-trimethoxy- $\beta$ -phenylpropio-phenone (IV); the filtrates containing the sugar residue were not examined. In a subsequent experiment the alkylation was stopped when a sample of the product no longer gave a ferric chloride reaction: a crystalline hydrate of trimethylphloridzin (III) was isolated which gave the ketone (IV) on hydrolysis. Methylation of phloridzin in a methyl-alcoholic-ethereal solution with diazo-methane and hydrolysis of the product also gave (IV).



The orientation of the ketone (IV) is established by ring closure with sodium acetate and acetic anhydride to the 1:4-benzopyrone (VI). The conclusion that this product is a benzopyrone and not a coumarin is based mainly on the behaviour of analogous ketones under the same conditions (Kostanecki and Różycki, *Ber.*, 1901, 34, 107; Crabtree and Robinson, J., 1918, 113, 859; Robinson and co-workers, J., 1929, 61, 152, which see for further references). Ciamician and Silber (*Ber.*, 1894, 27, 1627; 1895, 28, 1393), however, by acetylating phloretin, obtained a substance which they believed to be a coumarin. In any case ring closure can take place only if there is a hydroxyl group in the *o*-position to carbonyl in the hydroxytrimethoxy- $\beta$ -phenylpropio-phenone obtained by hydrolysis of the methylated glucoside. The constitution of phloridzin is therefore represented by formula (I).

The experimental proof of the constitutions of (VI) and of

Ciamician and Silber's product (*loc. cit.*) will be the subject of a future communication.

The compound (IV) was prepared by an independent method: condensation of phloroglucinol dimethyl ether and  $\beta$ -4-methoxy-phenylpropionitrile by the method of Hoesch produced a mixture of ketimine hydrochlorides which, on hydrolysis and separation, gave (IV) and the *isomeride* (V) in almost equal quantities.

Convenient methods for the preparation of *p*-methoxycinnamic acid (compare Perkin, J., 1877, **31**, 408; Einhorn, *Annalen*, 1883, **243**, 363; Knoevenagel, *Ber.*, 1898, **31**, 2606) and of  $\beta$ -4-methoxy-phenylpropionyl chloride (compare Barger and Walpole, J., 1909, **95**, 1723) are described. Dehydration of  $\beta$ -4-methoxyphenylpropionamide (Barger and Walpole, *loc. cit.*) with thionyl chloride gave the *nitrile*.

#### EXPERIMENTAL.

*Methylation of Phloridzin. Trimethylphloridzin.*—(A) Methyl iodide (14 c.c.) was added to a solution of phloridzin (15 g.) in dry acetone (80 c.c.) containing powdered potassium carbonate (25 g.) in suspension, and the mixture refluxed for 40 hours; a further quantity of iodide (28 c.c.) was added in two portions at intervals of 10 hours. After separation from potassium salts the mixture was acidified with acetic acid and the acetone and the excess of methyl iodide were removed by distillation. The pale straw-coloured viscous residue, which could not be crystallised, was insoluble in cold 10% alkali solution and did not give a ferric chloride reaction. A solution of the product in a mixture of 50% methyl alcohol (120 c.c.) and 15% sulphuric acid (50 c.c.) was refluxed for 20 minutes; on cooling, 6-hydroxy-2:4:4'-trimethoxy- $\beta$ -phenylpropiophenone (IV) separated, which crystallised from alcohol in colourless squat prisms (7.2 g.), melting at 110° [Found: C, 68.5; H, 6.3; OMe, 29.4.  $C_{18}H_{11}O_2(OMe)_3$  requires C, 68.3; H, 6.4; OMe, 29.4%]. This substance is slightly soluble in methyl alcohol and insoluble in warm water and in cold 2% aqueous sodium hydroxide solution. Ferric chloride added to an alcoholic solution gives a wine-red coloration. Acetylation with acetic anhydride and sodium acetate on the steam-bath during 3 hours gave the *acetyl* derivative, which separated from warm methyl alcohol in rhombic prisms, m. p. 62–63° (Found: C, 67.3; H, 6.2.  $C_{20}H_{22}O_6$  requires C, 67.0; H, 6.9%). It is readily soluble in warm alcohol and in ether, and does not give a ferric chloride reaction. Hydrolysis in alcohol with a little concentrated potassium hydroxide solution gave the parent ketone (III).

Phloridzin (10 g.) in acetone (50 c.c.) was methylated during 20

hours with methyl iodide and potassium carbonate. The product, isolated as before, solidified, but separated from warm benzene as an oil which gradually crystallised [Found in material dried at  $110^{\circ}$ : OMe, 20.7.  $C_{21}H_{21}O_7(OMe)_3$  requires OMe, 19.5%]. Repeated crystallisation from warm water (charcoal) gave a *monohydrate* of *trimethylphloridzin* (III) in colourless elongated prisms, m. p.  $63-65^{\circ}$  after softening at  $60^{\circ}$  [Found in material dried at  $110^{\circ}$ : C, 60.2; H, 5.9; OMe, 19.8.  $C_{21}H_{21}O_7(OMe)_3$  requires C, 60.2; H, 6.3; OMe, 19.5%. Found: loss on drying at  $110^{\circ}$ , 7.5. A monohydrate requires loss, 7.0%]. The hydrate is readily soluble in alcohol and does not give a ferric chloride reaction. Hydrolysis gave (IV), m. p. and mixed m. p.  $110^{\circ}$ .

(B) Diazomethane (3.5 g.) in dry ether (400 c.c.) was added to a solution of anhydrous phloridzin (5 g.) in absolute methyl alcohol (70 c.c.). A brisk evolution of nitrogen ensued and after 12 hours the ether and alcohol were removed under diminished pressure. The residual syrup, which was readily soluble in alcohol and in warm water and did not give a ferric chloride reaction, could not be crystallised. The crude product on hydrolysis with aqueous methyl-alcoholic sulphuric acid gave (IV), m. p. and mixed m. p.  $110^{\circ}$  after crystallisation from alcohol.

5 : 7 : 4'-Trimethoxy-3-benzyl-2-methyl-1 : 4-benzopyrone (VI).—A mixture of the ketone (IV) (6.5 g.), acetic anhydride (100 c.c.), and fused sodium acetate (40 g.) was heated at  $180^{\circ}$  for 16 hours. Water (400 c.c.) was then added to the cooled mixture and after 3 days the semi-solid product which had separated was extracted with ether. The *benzopyrone* (VI) remained as an insoluble residue, which crystallised from alcohol (charcoal) in clusters of colourless needles, m. p.  $165-166^{\circ}$  (Found: C, 70.7; H, 6.0.  $C_{20}H_{20}O_5$  requires C, 70.6; H, 5.9%). It is soluble in cold concentrated sulphuric acid to a colourless solution exhibiting a blue fluorescence in the light of a carbon arc, and in warm concentrated hydrochloric acid to a pale straw-coloured solution. An alcoholic solution is non-fluorescent.

The ether-soluble fraction of the reaction mixture consisted mainly of impure acetyltrimethylphlorethin, which, on being refluxed with acetic anhydride and sodium acetate at  $180^{\circ}$  for 18 hours, gave a further quantity of the benzopyrone, m. p.  $165-166^{\circ}$ .

$\beta$ -4-Methoxyphenylpropionamide.—A mixture of anisaldehyde (50 g.), malonic acid (45 g.), pyridine (150 c.c.), and piperidine (0.5 c.c.) was heated on the steam-bath for 9 hours and then under reflux for 2 hours. After dilution with water (400 c.c.) and acidification with concentrated hydrochloric acid (300 c.c.), it deposited *p*-methoxycinnamic acid (47 g.), which crystallised from alcohol in

colourless needles, m. p. 186—187° after sintering to an opaque mass at 169—171°. Reduction with sodium amalgam gave an almost theoretical yield of  $\beta$ -4-methoxyphenylpropionic acid, m. p. 101—103° (Perkin, *loc. cit.*).

$\beta$ -4-Methoxyphenylpropionyl chloride was prepared by warming a mixture of the acid (60 g.) and thionyl chloride (84 c.c.) on the steam-bath until the evolution of hydrogen chloride ceased. The excess of thionyl chloride was removed by distillation, the residual acid chloride dissolved in benzene (120 c.c.), and the solution saturated with ammonia; the amide (32 g.) then separated, m. p. 123—124° after crystallisation from water (compare Barger and Walpole, J., 1909, 95, 1723).

$\beta$ -4-Methoxyphenylpropionitrile.—A mixture of  $\beta$ -4-methoxyphenylpropionamide (31 g.) and thionyl chloride (45 c.c.) was heated under reflux for 1 hour. The excess of thionyl chloride was removed by distillation and an ethereal solution of the residue was washed with dilute sodium carbonate solution and then with water. The dried solution was freed from solvent and the resulting oil, on distillation under diminished pressure, gave the nitrile (16 g.) as a colourless oil, b. p. 172—173°/17 mm. (Found: C, 74.1; H, 7.0; N, 8.6.  $C_{10}H_{11}ON$  requires C, 74.5; H, 6.9; N, 8.7%).

*Condensation of  $\beta$ -4-Methoxyphenylpropionitrile with Phloroglucinol Dimethyl Ether.*—A solution of phloroglucinol dimethyl ether (13.8 g.) and  $\beta$ -4-methoxyphenylpropionitrile (14.5 g.) in dry ether (160 c.c.) was saturated with dry hydrogen chloride at 0° in the presence of anhydrous zinc chloride (7 g.). The mixed ketimine hydrochlorides separated as a semi-solid and after 4 days a further quantity was precipitated on the addition of dry ether (500 c.c.). A suspension of the mixture in water (250 c.c.) was heated on the steam-bath for 15 minutes; on cooling, the product solidified. Ethyl acetate extracted the ketone (IV) (6.5 g.), which crystallised from alcohol in squat prisms, m. p. and mixed m. p. 110° (Found: C, 68.2; H, 6.4%). Acetylation with acetic anhydride and sodium acetate at 100° gave the acetyl derivative, m. p. and mixed m. p. 62—63°. The latter, on being heated with acetic anhydride and sodium acetate at 180° for 18 hours, was converted into the benzopyrone (VI), which separated from warm alcohol in clusters of colourless needles, m. p. and mixed m. p. 165—166°.

The residue insoluble in ethyl acetate consisted of unchanged ketimine hydrochloride and was readily soluble in warm alcohol, from which it separated in colourless prisms on the addition of an excess of ethyl acetate. It was hydrolysed by boiling for 2 hours with water (300 c.c.). A solution of the solid product in cold 2%

aqueous sodium hydroxide (filtered to remove traces of insoluble impurities), on acidification with concentrated hydrochloric acid, gave 4-hydroxy-2:6:4'-trimethoxy- $\beta$ -phenylpropiophenone (V) (8 g.), which, on recrystallisation from 70% methyl alcohol and then from benzene, was obtained in colourless rectangular plates, m. p. 142° (Found: C, 68.2; H, 6.4.  $C_{18}H_{20}O_5$  requires C, 68.4; H, 6.3%). It is more readily soluble in alcohol and in benzene than the isomeric ketone (IV) and does not give a ferric chloride reaction. The acetyl derivative could not be crystallised.

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## VII.—The Nitration of Aromatic Thiocyanates.

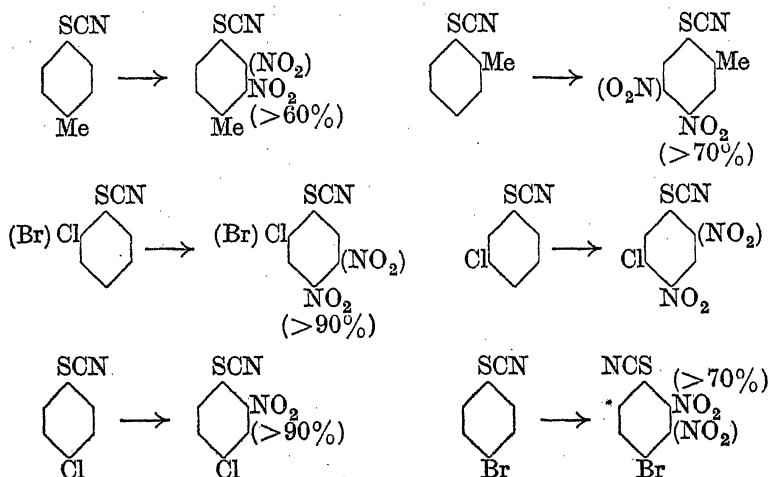
By FREDERICK CHALLENGER, CONSTANCE HIGGINBOTTOM, and  
ALFRED HUNTINGTON.

THE *o*:*p* ratio for the nitration of phenyl thiocyanate (Challenger and Collins, J., 1924, 125, 1377) has been found to be 1:4. The ratio for phenyl selenocyanate (Challenger and Peters, J., 1928, 1368), which is being determined, may be expected to be greater, since rise in the atomic number of the halogens increases ortho-substitution (Lapworth and Robinson, *Mem. Manchester Lit. Phil. Soc.*, 1927-8, 72, 49; *Ann. Rep.*, 1928, 141).

The preparation and nitration of *o*-chloro-, *o*-bromo-, and *m*-chloro-phenyl thiocyanates are now described. The ortho-compounds yielded almost exclusively 2-chloro(or bromo)-4-nitrophenyl thiocyanates. About 0.1 g. of the 5-nitro-derivative was obtained from 5.4 g. of *o*-chlorophenyl thiocyanate and from 5 g. of the *o*-bromo-compound. The results obtained in this and earlier communications are summarised on p. 27: the yield of mononitro-compound is recorded against the nitro-group, and the position of the nitro-group in the isomeride produced is shown by NO<sub>2</sub> in parentheses.

Both the thiocyano-group and the halogens, owing to their large number of unshared electrons, tend to transfer these to the carbon-sulphur or carbon-halogen linkage in phenyl thiocyanates or halogenobenzenes. A drift of electrons (conjugative effect) is thus set up which activates the *o*- and *p*-positions (Allan, Oxford, Robinson, and Smith, J., 1926, 409). The dissociation constants of

thiocyanoacetic acid (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 179) and of chloro- and bromo-acetic acids are  $2.65 \times 10^{-3}$ ,  $1.55 \times 10^{-3}$ , and  $1.38 \times 10^{-3}$  respectively. Thiocyanogen is therefore analogous to chlorine in attracting electrons more strongly than hydrogen and imposing on the benzene nucleus a positive field (negative general effect) which opposes the *o*:*p*-orienting conjugative effect. It is well known, however, that no meta-substitution has been detected with the halogenobenzenes, nor have we observed it with phenyl thiocyanate.



The results obtained on nitration of *p*-tolyl thiocyanate may be regarded as in agreement with the much greater ortho-directing influence of methyl as compared with that of thiocyanogen; the *o*:*p* ratio for  $\text{CH}_3$  is 58.8 : 36.8 and that of SCN is 20 : 80. Here in the major product the "general effects" of methyl (positive general effect) and of SCN support each other.

In *o*-tolyl thiocyanate, where the *p*-positions with respect to both substituents are unoccupied, the effect of SCN predominates. No vicinal derivatives such as  $\text{C}_6\text{H}_3(\text{NO}_2)(\text{SCN})(\text{CH}_3)[6:1:2]$  were isolated and the *o*-effects of SCN and  $\text{CH}_3$  appear to play a subordinate part. The result appears to be largely determined by the conjugative effect of SCN at position 4. Some substitution occurs to a less extent at 5, the position activated by the methyl group and least inhibited by the general effect of SCN.

With *o*-chloro- and *o*-bromo-phenyl thiocyanates examination shows no trace of vicinal derivatives in the nitration products. The conjugative effect of SCN and the general effect of halogen both tend to favour substitution at position 4, and only traces of

the 5-nitro-compounds are formed. With *m*-chlorophenyl thiocyanate vicinal substitution is again absent and two products are formed by the reinforced conjugative effects of SCN and chlorine at positions 4 and 2 respectively, the 4-nitro-compound predominating.

The most interesting feature of these results is the relation of the effects induced by SCN to those induced by methyl and chlorine. It appears from the nitration of the tolyl thiocyanates that the speeds of substitution induced by the CH<sub>3</sub> and the SCN group are not very different, since in comparing ortho-effects (*p*-tolyl thiocyanate) methyl predominates, and in comparing para-directing effects (*o*-tolyl thiocyanate) SCN predominates. On the other hand, the results for halogenophenyl thiocyanates clearly show that the speeds of substitution *o*- or *p*- to SCN are incomparably greater than those *o*- or *p*- to chlorine or bromine in these molecules. In Holleman's series OH > NH<sub>2</sub> > I > Cl > Br > CH<sub>3</sub>, chlorine is slightly more powerful than methyl (compare Challenger and Collins, *loc. cit.*). Further work is in progress and a study of the physical properties of certain thiocyanates will be made. Attempts to prevent elimination of iodine on nitration of *p*-iodophenyl thiocyanate were unsuccessful (compare Challenger and Collins, *loc. cit.*; Körner, *Gazzetta*, 1875, 4, 385; Mayes and Turner, J., 1928, 691).

Ingold, Smith, and Vass (J., 1927, 1245) showed that the decomposition of substituted aryl iododichlorides to chloriodobenzenes is an intermolecular reaction, the position entered by chlorine being determined not necessarily by the iodine, but by the strongest group present. Attempts to decompose the *dichloride* of *p*-iodophenyl thiocyanate so as to induce nuclear chlorination failed, loss of chlorine and regeneration of the iodothiocyanate usually occurring. In sunlight *pp'*-di-iododiphenyl disulphide was formed. This decomposition possibly proceeds by liberation of cyanogen chloride and formation of the *p*-iodophenyl thiolchloride I·C<sub>6</sub>H<sub>4</sub>·SCl. Thiols of this type yield disulphides with alcohol. It has therefore been impossible to compare the orienting effects of iodine and thiocyanogen.

Our results may be compared with those of Werner (J., 1907, 91, 240, 529), who found that a nitro-group in the *o*- or *p*-position to ICl<sub>2</sub> prevents nuclear chlorination. With a halogen atom in the *p*-position, this effect is slightly less, some nuclear chlorination taking place.

#### EXPERIMENTAL.

*o*-Chlorophenyl Thiocyanate.—*o*-Chloroaniline was diazotised at 0°, added to an aqueous solution of ferric chloride and potassium thiocyanate, and left over-night. The *thiocyanate* was extracted



twice with benzene, distilled in steam, and again extracted with benzene. After three fractionations in a vacuum it was almost colourless, boiled at  $160\text{--}160.5^\circ/42\text{--}47$  mm., and solidified in ice. Yield, 18 g. (53% of the theoretical). It has an unpleasant odour and the vapour attacks the eyes and skin (Found: Cl, 20.7, 21.1; S, 19.1, 19.15.  $\text{C}_7\text{H}_4\text{NClS}$  requires Cl, 20.9; S, 18.9%).

The *o*-bromo-, *p*-iodo-, and *m*-chloro-derivatives of phenyl thiocyanate were similarly prepared (see table below). Extraction with benzene prior to steam distillation removes inorganic salts which may facilitate disulphide formation during treatment with steam.

The irritant effect of *m*-chlorophenyl thiocyanate is much more pronounced than that of the other halogen derivatives.

**2-Chloro-4-nitrophenyl Thiocyanate.**—2-Chloro-4-nitroaniline was obtained by the method of Chattaway, Orton, and Evans (*Ber.*, 1900, **33**, 3061), but hot dilute sulphuric acid was found to be most suitable for hydrolysis of the 2-chloro-4-nitroacetanilide, the free base separating on cooling.

2-Chloro-4-nitroaniline was diazotised at  $-5^\circ$  and treated as described above. The *product*, when crystallised from alcohol, acetone and finally from light petroleum, formed colourless needles, m. p.  $85^\circ$  (Found: N, 13.3.  $\text{C}_7\text{H}_3\text{O}_2\text{N}_2\text{ClS}$  requires N, 13.05%).

The other halogenonitro-thiocyanates were prepared similarly (see table), cuprous thiocyanate being occasionally employed in place of ferric chloride.

2-Chloro-5-nitrophenyl thiocyanate melts at  $107^\circ$  (Found: C, 39.6; H, 1.3.  $\text{C}_7\text{H}_3\text{O}_2\text{N}_2\text{ClS}$  requires C, 39.2; H, 1.4%).

Substituted aniline.	Wt. of base (g.).	$\text{H}_2\text{SO}_4$ (c.c.).	Water (c.c.).	$\text{NaNO}_2$ (g.).	KSCN (g.).	$\text{Cu}_2(\text{SCN})_2$ (g.).	$\text{FeCl}_3$ (g.).	M. p. or b. p. of product.
2-Cl	25.5	40	160	18.7	38.8	—	30	B. p. $160^\circ/42$ mm.
2-Br	30	40	160	18.0	38.0	—	63.6	B. p. $161\text{--}165^\circ/10\text{--}12$ mm.
3-Cl	40	54	200	25.0	60.0	—	30.0	B. p. $135^\circ/12.5$ mm.
4-SCN	5	3.9	86	3.0	9 g. KI	—	—	M. p. $53^\circ*$
2-Cl-5- $\text{NO}_2$	10	60	120	5.0	12.0	—	10.0	$107^\circ$
2-Cl-4- $\text{NO}_2$	1.7	20	40	0.9	1.9	—	1.6	" $85^\circ$
2-Br-5- $\text{NO}_2$	2.5	15	30	1.1	1.5	2.0	—	" $124.5^\circ$
2-Br-4- $\text{NO}_2$	1.0	8	16	0.5	0.6	0.8	—	" $93^\circ$
3-Cl-4- $\text{NO}_2$	6.0	100	100	3.0	6.2	—	5.3	" $59^\circ$
3-Cl-6- $\text{NO}_2$	6.0	100	100	3.0	6.2	—	5.3	" $104.5^\circ$

The product contained SCN in place of the  $\text{NH}_2$  of the original base in every case except that marked \*, where *p*-iodophenyl thiocyanate was formed.

**Nitration of *o*-Chlorophenyl Thiocyanate.**—The thiocyanate (5.4 g.) was slowly added to well-stirred nitric acid (*d* 1.5; 18 c.c.) at  $-6^\circ$ , left for 4 hours at room temperature, and poured on ice. The crude

product, m. p. 76—78°, weighed 6.6 g., i.e., 96% of the amount required for a mononitro-derivative. Fractional crystallisation from alcohol and then from light petroleum gave a main product (A), m. p. 85°, and about 0.01 g. of (B), m. p. 107°.

A and B did not depress the m. p.'s of synthetic specimens of 2-chloro-4-nitrophenyl thiocyanate and of 2-chloro-5-nitrophenyl thiocyanate respectively (Found for A: Cl, 16.6; S, 14.7; N, 13.3. Found for B: N, 13.2.  $C_7H_3O_2N_2ClS$  requires Cl, 16.5; S, 14.9; N, 13.05%).

A was boiled with animal charcoal in alcohol: the solution yielded a small quantity of white crystals (E), m. p. 165°, which were less soluble in alcohol and gave no thiocyanate reaction. Since (A) was previously pure, the formation of sulphide or disulphide was suspected and the behaviour of synthetic 2-chloro-4-nitrophenyl thiocyanate towards charcoal was studied. The production of E was confirmed and shown to be due to the charcoal and not to the alcohol. The charcoal gave an alkaline reaction in water. After being boiled with hydrochloric acid and washed, it was found not to affect the thiocyanate even when boiled for several hours in alcohol. When the thiocyanate was left with 10% sodium hydroxide solution for 7 days and recrystallised from acetone, the same product ( $E_1$ ), m. p. 165, was obtained, as also on treatment with warm alcoholic ammonium sulphide ( $E_2$ ). The m. p. of E was not depressed on admixture with  $E_1$  or  $E_2$ . The method of formation of  $E_2$  shows it to be a disulphide (compare Müller, *Z. farb. Text. Ind.*, 1906, 5, 357), a conclusion confirmed by the formation of diphenyl disulphide, m. p. and mixed m. p. 60°, and of di-*o*-nitrophenyl disulphide from the corresponding thiocyanates and sodium hydroxide. *o*-Nitrophenyl thiocyanate also gave the disulphide when boiled with the contaminated charcoal in alcohol.

*Preparation and Nitration of o-Bromophenyl Thiocyanate.*—(a) The preparative details are given on p. 29. The product formed white needles, m. p. about 24° (Found: S, 14.9, 14.8; Br, 37.65.  $C_7H_4NBrS$  requires S, 14.95; Br, 37.3%). (b) The thiocyanate (5 g.) was added during 45 minutes to nitric acid (*d* 1.5; 18 c.c.) at -5° to -6°, left at room temperature for 15 minutes, and poured on ice. The yield of crude product, m. p. about 83°, was 5.8 g. (97% of the amount required for a mononitro-derivative). Fractional crystallisation from alcohol and from light petroleum gave a main product (C), m. p. 93°, and a trace of (D), m. p. 126°. These did not depress the m.p.'s of synthetic specimens of the 4-nitro- and 5-nitro-2-bromophenyl thiocyanates respectively (Found for C: N, 11.0; Br, 31.0, 30.9. Found for D: N, 11.0.  $C_7H_3O_2N_2BrS$  requires N, 10.8; Br, 30.9%).

**2-Bromo-4-nitrophenyl Thiocyanate.**—2-Bromo-4-nitroaniline was prepared from *o*-bromoacetanilide and nitric acid (*d* 1.5) at  $-5^{\circ}$  to  $-10^{\circ}$ . Having been kept for 30 minutes in the freezing mixture and for  $1\frac{1}{2}$  hours at room temperature, the reaction mixture was treated with ice. The solid obtained, m. p.  $120^{\circ}$ , was fractionally crystallised: the less soluble portion, m. p.  $130^{\circ}$  (Chattaway, Orton, and Evans, *loc. cit.*, give  $129^{\circ}$  as the m. p. of 2-bromo-4-nitroacetanilide), was treated for  $1\frac{1}{2}$  hours with sulphuric acid at  $100^{\circ}$  and poured into water, giving the yellow base, m. p.  $105^{\circ}$  (Hübner, *Ber.*, 1877, 10, 1709, gives m. p.  $104.5^{\circ}$ ). The preparation by this method has not been described.

The *thiocyanate* was prepared as usual (see p. 29). It formed pale yellow crystals, m. p.  $93^{\circ}$ , from light petroleum and gave the thiocyanate reaction (Found: N, 10.9.  $C_7H_3O_2N_2BrS$  requires N, 10.8%).

**2-Bromo-5-nitrophenyl Thiocyanate.**—The corresponding amine was prepared by the method used by Chattaway, Orton, and Evans (*loc. cit.*) for the chloro-derivative, the application of which to the bromo-compound does not appear to be described. The pale yellow *thiocyanate* (see p. 29), after crystallising from alcohol and finally from light petroleum, melted at  $126^{\circ}$  (Found: C, 32.6; H, 1.5.  $C_7H_3O_2N_2BrS$  requires C, 32.4; H, 1.16%).

**Preparation and Nitration of *m*-Chlorophenyl Thiocyanate.**—(a) See p. 29 for preparative details. Shortly after the addition of the *m*-chlorobenzenediazonium chloride to the ferric thiocyanate there was a violent reaction and the temperature rose considerably. This was also observed in a second experiment when the mixture was standing in ice. The pure *thiocyanate* boiled at  $135^{\circ}/12.5$  mm. (Found: N, 8.6.  $C_7H_4NClS$  requires N, 8.3%).

(b) The *thiocyanate* (5 g.) was slowly added to well-stirred nitric acid (*d* 1.5; 15 c.c.) at  $-10^{\circ}$ . After an hour the liquor was left at room temperature for 2 hours and poured on ice. Fractional crystallisation of the washed and dried crude product (5.9 g., m. p.  $44-48^{\circ}$ ) from ethyl alcohol and then from methyl alcohol yielded (F), m. p.  $48-51^{\circ}$ , and (G), m. p.  $104^{\circ}$ . Crystallisation of F did not alter the m. p. Distillation with steam failed to purify it, since the product ceased to give the thiocyanate reaction (Challenger and Peters, *J.*, 1928, 1368) and melted at  $130-135^{\circ}$ . Repetition of the nitration and further crystallisation from light petroleum finally gave a large fraction (H), m. p.  $59^{\circ}$ , and a very small one (K), m. p.  $104-105^{\circ}$ . There was no evidence of any other isomeride. H and K did not depress the m.p.'s of the thiocyanates of the same melting points prepared from 3-chloro-4-nitroaniline and 3-chloro-6-nitroaniline, respectively (Found for H and K: N, 13.2 and 13.1 respectively.  $C_7H_3O_2N_2ClS$  requires N, 13.05%).

*Preparation of the 6- and the 4-Nitro-derivative of m-Chlorophenyl Thiocyanate.*—The corresponding amines were prepared by the method of Mayes and Turner (J., 1928, 693). The 6-nitro-thiocyanate, after crystallising from ethyl alcohol and twice from methyl alcohol, melted at 104–105° (Found : Cl, 16.2, 16.7; N, 13.3; S, 14.6). The 4-nitro-compound, m. p. 59°, was crystallised first from alcohol and then from light petroleum (Found : N, 13.3, 13.2.  $C_7H_3O_2N_2ClS$  requires N, 13.05; Cl, 16.5; S, 14.9%).

*Preparation and Attempted Nitration of p-Iodophenyl Thiocyanate.*—This substance was obtained by Challenger and Collins (*loc. cit.*), but was not analysed. It melts at 53° (Found : I, 48.3; S, 11.9.  $C_7H_4NIS$  requires I, 48.5; S, 12.3%).

*p*-Iodophenyl thiocyanate was attacked neither by nitric acid (*d* 1.41) at  $-10^\circ$  or at  $15^\circ$ , nor, in acetic anhydride solution, by nitric acid (*d* 1.5) at  $0^\circ$ . On slow addition of the thiocyanate (1 g.) to a mixture of sulphuric acid (10 c.c.) and nitric acid (*d* 1.41; 10 c.c.) at  $-14^\circ$ , most of it dissolved, forming a pale brown solution, but iodine did not appear to be liberated. After remaining for 3 hours at  $-10^\circ$  to  $-5^\circ$ , the mixture was poured on ice; a black solid then separated, becoming paler in air and giving only *p*-nitrophenyl thiocyanate, m. p. and mixed m. p.  $133^\circ$ , on fractional crystallisation. The acid liquor contained free iodine. Similar results were obtained with nitric acid (*d* 1.5) at  $-16^\circ$ . With equal volumes of nitric acid (*d* 1.5) and (*d* 1.41) at  $-12^\circ$ , reaction was very slow, but on addition of more acid (*d* 1.5) a black solid separated. The *p*-nitro-derivative was isolated as before.

*Preparation of p-Dichloriodophenyl Thiocyanate.*—The iodothiocyanate in three times its weight of chloroform was cooled in ice and treated with chlorine for about 30 minutes and the pale yellow needles were washed with light petroleum; m. p.  $111^\circ$ . The substance was analysed by Willgerodt's method ("Die Organischen Verbindungen mit mehrwertigem Jod," 1914, p. 22) using potassium iodide and sodium thiosulphate (Found : Cl, 21.4, 21.3.  $C_7H_4NCl_2IS$  requires Cl, 21.4%).

When heated in an open vessel to  $100^\circ$ , the iododichloride evolved chlorine. The solidified residue, m. p.  $49^\circ$ , had m. p.  $51^\circ$  after recrystallisation and did not depress the m. p. of *p*-iodophenyl thiocyanate ( $52-53^\circ$ ). The thiocyanate was also formed in (a) boiling carbon tetrachloride and (b) light petroleum (b. p.  $40-50^\circ$ ); addition of iron filings to (a) did not affect the result. After remaining for 24 hours in ultra-violet light, the iododichloride was completely converted into the thiocyanate. The iododichloride (3 g.), exposed to sunlight in a closed bottle, liquefied after 2 weeks but became solid a few days later. Much pressure developed,

hydrogen chloride was present, and a very pungent odour which may have been that of cyanogen chloride. The yellow solid produced melted at 53°; after recrystallisation from alcohol, it became colourless, melted at 126°, and did not depress the m. p. (126°) of *pp'*-di-iododiphenyl disulphide.

*Preparation of Phenyl Thiocyanate and Quantitative Study of its Nitration.*—Challenger and Collins (*loc. cit.*) prepared phenyl thiocyanate by Gattermann's method (*Ber.*, 1890, **23**, 738), using potassium and cuprous thiocyanates. A better yield is obtained with ferric chloride and potassium thiocyanate (Korczyński, *Bull. Soc. chim.*, 1922, **31**, 1179), although in this and other cases (see p. 31) the evolution of nitrogen tends to lag and then suddenly to become violent. The steam-distilled product was carefully fractionated; b. p. 143—145°/64 mm. (Found: S, 23·4, 23·3. Calc.: S, 23·7%). Phenyl mercaptan and phenyl disulphide, which are possible impurities, contain 29·1 and 29·3% of sulphur respectively).

The *o*-, *m*-, and *p*-nitro-thiocyanates required for thermal analysis were prepared by the diazo-reaction (Müller, *Z. farb. Text. Ind.*, 1906, **5**, 357) by means of copper salts. Steam distillation was impracticable and the thiocyanates were purified by extraction of the solid product with alcohol and decoloration with carefully purified charcoal.

*Nitration of phenyl thiocyanate.* The thiocyanate (10 g.) was slowly added to nitric acid (*d* 1·41; 24 c.c.) and sulphuric acid (27 c.c.) at 0—5°. After 5 g. had been added, a solid separated. After remaining for 5 hours at 0°, the mixture rose to room temperature, but, as the odour of phenyl thiocyanate was still perceptible, another 6 c.c. of each acid were added. After 4 hours, the mixture was poured on ice, thiocyanate odour being absent. The oil-free solid was washed, triturated with cold water, shaken with water for several hours, dried at about 90°, and left in a desiccator. Yield, 12·5 g. (94% of the theoretical yield for a mononitro-derivative). The washings and spent acid were extracted with benzene, but yielded only a small amount of oil with an odour of phenyl thiocyanate. The nitration product was examined for compounds other than *o*- and *p*-nitrophenyl thiocyanates. When fused, it had a very slight odour of phenyl thiocyanate. The smell of this substance is very powerful and only minute traces could have been present. Repeated fractionation failed to detect any *o*- or *p*- or dinitro-derivative of phenyl disulphide which might have been produced by oxidation of the nitro-thiocyanates. These substances are difficultly soluble. A test was made for the presence of 2 : 4-dinitrophenyl thiocyanate. Addition of *o*- or *p*-nitrophenyl thiocyanate to a mixture of acetone and sodium hydroxide gives an orange colour to the acetone layer, the

alkali being coloured pale yellow. A trace of the dinitro-compound colours the mixture almost black and the alkali red. With the nitration mixture the colour was orange-yellow, indicating the absence of the dinitro-derivative.

*Thermal analysis of the nitration mixture.* The setting point (S.P.) of the well-washed and dried nitration mixture was  $121.9^{\circ}$ , results differing by not more than  $0.1^{\circ}$  being obtained on remelting. A second nitration of phenyl thiocyanate gave a product of S.P.  $121.7^{\circ}$ . The eutectic point was difficult to observe but appeared to be about  $95^{\circ}$ . The S.P. of various mixtures of *o*- and *p*-nitrophenyl thiocyanates were then determined by adding increasing quantities of the *o*-derivative to the *p*-compound of S.P.  $131.0^{\circ}$ .

% Ortho- .....	1	2	4	6	10
S.P. ....	$130.3^{\circ}$	$129.5^{\circ}$	$128.5^{\circ}$	$127.6^{\circ}$	$126.1^{\circ}$
% Ortho- .....	15	20	21	30	
S.P. ....	$124.0^{\circ}$	$121.9^{\circ}$	$121.5^{\circ}$	$114.5^{\circ}$	

From these figures the nitration product would appear to contain 20% of *o*-nitrophenyl thiocyanate. The eutectic point of one of the synthetic mixtures was found to be about  $96.5^{\circ}$ , in fairly good agreement with that of the nitration product.

The nitration product being assumed to consist solely of 80% of para- and 20% of ortho-thiocyanate, sufficient *o*-nitrophenyl thiocyanate was added to form a 30% mixture. The S.P. was  $114.9^{\circ}$ , and that of a synthetic mixture is  $114.5^{\circ}$  (see table), the results being therefore in agreement. Further evidence was afforded by examination of mixtures containing *m*-nitrophenyl thiocyanate. A synthetic mixture containing 76.2% of para-, 19.0% of ortho-, and 4.8% of meta- had S.P.  $118.6^{\circ}$ . On addition of 0.2094 g. of *m*-nitrophenyl thiocyanate to 4.1870 g. of the nitration product, the resulting mixture should contain 4.8% of meta-. The observed S.P. was  $118.9^{\circ}$ .

Part of the cost of this investigation was defrayed by a grant from the Research Fund of the Chemical Society, for which the authors desire to express their thanks.

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VIII.—*The Parachor of Chlorine Dioxide.*

By GEOFFREY HERBERT CHEESMAN.

THE structure of chlorine dioxide,  $\text{ClO}_2$ , has always been the subject of much speculation, and the electronic ideas of valency do not solve the difficulty, for the total electron content (19 outer-sheath electrons)

is an odd number. As usual with inorganic compounds, it is difficult to obtain evidence of structure, but in this case it seemed reasonable to try Sugden's parachor method. Chlorine dioxide, being liquid between  $-59^\circ$

and  $+10^\circ$  under atmospheric pressure, is suitable for surface-tension and density measurements. Through-

out this work the chlorine dioxide-carbon dioxide mixture produced by Bray's method was frozen out and fractionated.

Quantities of liquid up to about 1 c.c. were condensed and fractionated in the simple vacuum apparatus shown in Fig. 1. The material was condensed in A, and warmed to  $0^\circ$ , whereupon all the carbon dioxide passed off. About one-quarter of the liquid was allowed to evaporate away through tap D. The remainder was frozen out, the apparatus pumped out, and two-thirds of the remainder distilled

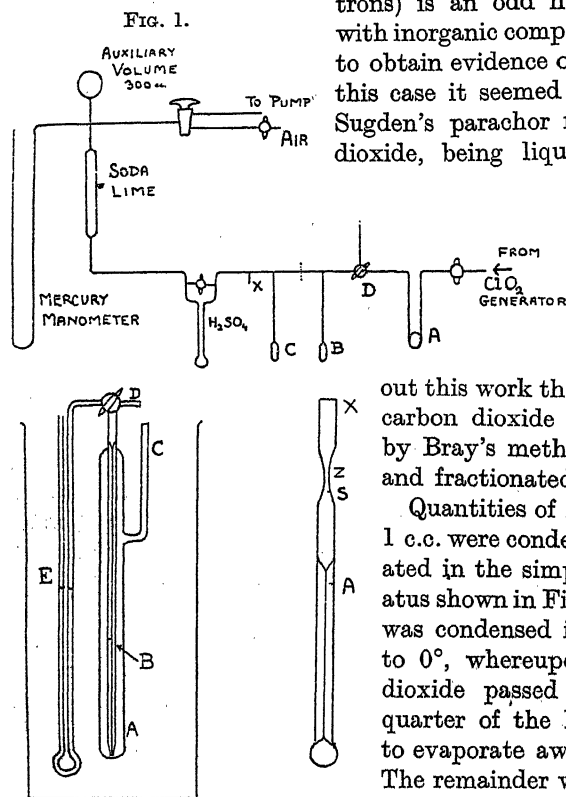


FIG. 2a.

FIG. 2b.

into B by surrounding the latter with liquid air. From this, one-quarter was again rejected, and the middle portion distilled as before into C. All the material was then frozen in liquid air, and the apparatus evacuated and sealed between C and B. About 0.2–0.4 c.c. was thus obtained.

The purity of the material was followed by vapour-pressure determinations with the mercury manometer and sulphuric acid buffer on the left of the apparatus. Reproducible pressures were obtained

in good agreement with those of King and Partington (J., 1926, 925).

Two sets of density determinations were made, the first by a method of balancing columns, and the second by a pycnometer method. The first method is illustrated by Fig. 2*a*. The inner tube of the apparatus, B, was a uniform capillary, and the material was distilled into the lower portion of A through the side tube C. Suction was gently applied at D, and the heights of the liquid in the capillary and of the water in the U-tube E were measured with a sliding microscope. About 20 readings were taken, and the height of liquid plotted against the height of water. The points lay on a straight line, the gradient of which gave the relative density of the liquid at the temperature of the experiment (0°).

Two experiments on these lines gave rather different results, and hence the second method was tried. The actual pycnometer resembled a small thermometer (Fig. 2*b*) with a mark at A on the capillary stem, and a file scratch at S; it was sealed to the fractionation apparatus at X. Sufficient material was distilled in to fill it nearly to A when at 0°, and then frozen out. The apparatus was evacuated, sealed off at Z, and maintained at 0° till the meniscus remained steady, and the distance below A was measured with the sliding microscope. (Further readings at other temperatures gave the corresponding densities, which it is hoped to communicate later.) The instrument was then weighed, the contents frozen, and the apparatus carefully broken open at S, any small fragments (which were only produced on one occasion) being retained. The contents were allowed to evaporate, the apparatus dried in a vacuum, and reweighed. A previous calibration with mercury gave the volume to the mark A and the volume per mm. of stem below the mark. Hence the density of the liquid could be calculated. The densities (g./c.c. at 0°) obtained by the two methods were as follows, the mean of all five determinations being 1.642.

Balanced-column method: 1.622, 1.645. Pycnometer method: 1.661, 1.639, 1.644.

The surface tension was measured by capillary rise, the mean of seven consistent experiments in different apparatus giving  $\gamma/D = 20.1$ . Combination of this with the density above gives the surface tension as 33.1 dynes/cm. at 0°, and hence the parachor is 98.7 units.

The data of King and Partington (*loc. cit.*) and cryoscopic measurements of Bray (*Z. physikal. Chem.*, 1906, 54, 569) appear to indicate absence of association, and a determination in the present work of the Ramsay-Shields coefficient confirms this. (The experiments upon the surface tension, density, and other properties at lower temperatures will be published later.) The determined parachor



may therefore be compared with the sum of the atomic parachors of the elements, *viz.*, 94.3, leaving a structural parachor of +4.4 units.

On the assumption that all octets are completed, there are eleven possible electron distributions for chlorine dioxide. Of these, three do not yield readily calculable parachors, but are improbable on account of large polarities accumulated on single atoms; five others are unlikely because they give large negative structural constants. The remaining three are shown below :

(I.)	$\begin{array}{c} -\frac{1}{2} \quad +1 \quad -\frac{1}{2} \\ \text{O}=\text{Cl}=\text{O} \\ \boxed{\phantom{000}} \end{array}$	(II.)	$\begin{array}{c} +\frac{1}{2} \quad -\frac{1}{2} \\ \text{Cl}=\text{O}=\text{O} \\ \boxed{\phantom{000}} \end{array}$	(III.)	$\begin{array}{c} -\frac{1}{2} \quad +\frac{1}{2} \\ \text{Cl}-\text{O}\equiv\text{O} \\ \boxed{\phantom{000}} \end{array}$
2 Semipolar double bonds	- 3.2	Semipolar singlet	- 12.4	Semipolar singlet	- 12.4
Non-polar singlet .....	- 11.6	3-Membered ring	+ 17.0	Double bond	+ 23.2
3-Membered ring .....	+ 17.0	Structural const.	+ 4.6	Structural const.	+ 10.8
Structural const. ....	+ 2.2				

On the assumption that formula (I) contains only one integral dipole, the structural parachor amounts to +3.6 units. Formulæ (I) and (II) therefore give the closest agreement with the observed value, and further work is now in hand to adduce other evidence for the structure of the dioxide and other halogen oxides. The structure (II) herein suggested appears somewhat novel, but accords quite well with the known reactions of the oxide.

The work was carried out in the laboratory of Professor Baker, and thanks are due to him for his interest in it.

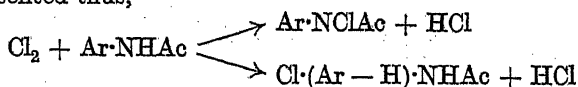
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## IX.—*The Chlorination of Anilides. Part VI. The Rates of N-Chlorination of Acetanilides and Acetobenzylamides and the Effects of Substituents upon Side-chain Reactivity.*

By GWYN WILLIAMS.

IN a previous paper (Orton, Soper, and Williams, J., 1928, 998) a method was described for measuring the rates of reaction of anilides with chlorine in aqueous acetic acid media and Wegscheider's test was applied to show that *N*-chlorination and *C*-chlorination proceed simultaneously, so that, under these conditions, the reactions may be represented thus,



The ratio  $k_N/k_C$  (where  $k_N$  and  $k_C$  are the velocity coefficients for

*N*- and *C*-chlorination respectively) is constant for each anilide throughout the reaction, but varies widely for different anilides, having the values 0.00873, 0.0548, 0.850, 10.40 for acetanilide and *m*-, *p*-, and *o*-chloroacetanilides respectively in 40% acetic acid, whilst *N*-chlorination predominates in nitroacetanilides and acetobenzylamides with almost complete exclusion of simultaneous *C*-chlorination. The object of this paper is to consider the influence of the substituents NO<sub>2</sub>, Cl, and CH<sub>3</sub> upon the rates of these reactions, with special reference to the *N*-chlorination which takes place in 40% acetic acid and aqueous media (Soper, *J. Physical Chem.*, 1927, 31, 1192) but is absent under the conditions prevailing in other investigations of the rates of chlorination of anilides (Orton and King, *J.*, 1911, 99, 1369; Orton and Bradfield, *J.*, 1927, 986). The influence exerted by substituents in the benzene nucleus upon side-chain reactivity is closely allied to the general problem of orientation, and the above substituents have been chosen so as to furnish a contrast in orienting activities, those of NO<sub>2</sub> and CH<sub>3</sub> being opposed, whilst the action of Cl depends upon whether its "tautomeric" or its "inductive" influence has the greater scope.

Table I gives the results for 22 anilides. Each value is the average of three or more experiments\* and the mean deviation from the mean is estimated, in general, at  $\pm 2-3\%$ ; it is often less than this (see Orton, Soper, and Williams, *loc. cit.*) and never more than 5%. Where no value is given for  $k_c$ , nuclear chlorination is too slow in comparison with *N*-chlorination to be distinguished with certainty from accidental loss of chlorine. The figures in parentheses are subject to qualifications discussed in the experimental section.

TABLE I.

Temp. 18° ( $\pm 0.02^\circ$ ). Medium, 40% acetic acid (6.90*N*).

Acetanilide	$k_N$ .	$k_C$ .	Acetobenzylamide...	$k_N$ .
Substituent:	96	11,000	Substituent:	172
<i>o</i> -NO <sub>2</sub> .....	550	—	<i>o</i> -NO <sub>2</sub> .....	16.1
<i>m</i> -NO <sub>2</sub> .....	87	—	<i>m</i> -NO <sub>2</sub> .....	32.9
<i>p</i> -NO <sub>2</sub> .....	60	—	<i>p</i> -NO <sub>2</sub> .....	27.7
† 2:4-Di-NO <sub>2</sub> .....	—	—		
<i>o</i> -Cl .....	286	28	<i>o</i> -Cl .....	28.9
<i>m</i> -Cl .....	172	3,140	<i>m</i> -Cl .....	63.5
<i>p</i> -Cl .....	115	135	<i>p</i> -Cl .....	99
2:4-Di-Cl .....	504	—		
<i>o</i> -CH <sub>3</sub> .....	140	1,390		
<i>m</i> -CH <sub>3</sub> .....	(150)	(50,000)		
<i>p</i> -CH <sub>3</sub> .....	2540	18,500	<i>p</i> -CH <sub>3</sub> .....	(285)
Aceto- $\beta$ -phenylethylamide .....				205
Acetamide .....				(237)

† Chloroamine equilibrium unsuitably placed.

\* I am indebted to Mr. S. P. Hughes, B.Sc., for help in checking values for three substances.

The electronic theory has recently been applied to the classification of benzene side-chain reactions (*Ann. Reports*, 1927, 1928) and, with certain reservations (see below), it may be used to interpret Table I, which illustrates the effects of substituents upon the speed of *N*-chlorination for a particular set of conditions. To this end, Table II has been constructed so as to investigate (a) how far the effects of substituents are consistent in a number of side-chain reactions; (b) whether, if consistency is found, it is such as to support the electronic schemes; (c) to determine whether *N*-chlorination finds a place in the scheme; (d) to seek analogies in other reactions for certain peculiarities observed in *N*-chlorination.

Table II gives the effects of the substituents  $\text{NO}_2$ ,  $\text{Cl}$ , and  $\text{CH}_3$  upon 36 reactions, the rates for each reaction being calculated relative to that for the unsubstituted compound as unity. Only those reactions are included in which more than one substituent has been investigated.

The electronic theory suggests that it should be possible to group side-chain reactions in two main classes accordingly as they are favoured by accession of electrons to the point of reaction or by recession from that point. The influence of  $\text{CH}_3$  should be in the opposite sense to that of  $\text{NO}_2$  and  $\text{Cl}$  (if its inductive influence is predominant), and superimposed on these general effects there should be alternating effects where the substituent can initiate covalency changes. Table II shows that a general measure of consistency exists in the effects of groups in accelerating or retarding side-chain reactions and that the reactions tabulated fall into two main groups; 19 are in Group A with the nitro-group accelerating and the methyl group retarding, and 12 are in Group B, in which the reverse holds. It has been observed in drawing up the table that other substituents fall into line with those tabulated, the same sharp contrast existing between those which are *op*- and those which are *m*-directing in the usual substitution reactions. Five reactions (Group C) cannot be allotted with certainty to either class.

In the following scheme the alternating effects suggested by theory are compared with those observed :

Group A.			Group B.		
	$-\text{NO}_2 > \text{H} > -\text{CH}_3$ .	Agree- ment.	$-\text{CH}_3 > \text{H} > -\text{NO}_2$ .	Agree- ment.	
For $-\text{NO}_2$	<i>m</i> -<(o) <i>p</i> -	7 out of 9	<i>m</i> ->(o) <i>p</i> -	7 out of 8	
For $-\text{CH}_3$	<i>m</i> ->(o) <i>p</i> -	7 out of 9	<i>m</i> -<(o) <i>p</i> -	8 out of 9	

There are also many instances, not included in Table II, of alternating effects in the expected sense when only one substituent has been investigated. In Group C of Table II, also, the alternating effects for a given substituent are generally as anticipated. It is seen in

TABLE II.

Group A.	<i>o</i> -NO <sub>2</sub>	<i>m</i> -NO <sub>2</sub>	<i>p</i> -NO <sub>2</sub>	<i>o</i> -Cl	<i>m</i> -Cl	<i>p</i> -Cl	H	<i>o</i> -CH <sub>3</sub>	<i>m</i> -CH <sub>3</sub>	<i>p</i> -CH <sub>3</sub>	Medium.
5	—	—	—	1.8	1.2	1.6	1	—	Small?	—	Glacial acetic acid
6	—	3.01	—	—	—	—	1	—	—	0.736	Aq. acetone
7	—	1.85	—	—	—	—	1	—	—	0.917	Aq. alcohol
12	—	17.2	17.7	3.44	3.17	1.74	1	3.32	—	0.567	Alcohol
13	Large	1.37	Large	1.05	1.00	1.02	1	0.389	0.857	0.953	Water
14	"	1.70	"	0.07	1.03	0.96	1	0.222	0.981	0.973	"
16	—	11.7	—	8.00	1.40	1.69	1	0.862	1.42	0.713	"
18	8.20	3.90	3.45	8.84	6.09	7.73	1	(0.373	0.485	0.494)	Alcohol
26	1.03	3.27	2.43	1.16	—	1.71	1	0.506	1.01	0.946	Methyl alcohol
27	1.99	5.82	4.07	—	—	1.16	1	0.089	—	0.370	"
28	—	—	—	1.13	1.93	1.19	1	0.419	0.465	0.448	"
29	—	Very large	—	2.89	8.94	3.83	1	0.247	0.746	0.507	Alcohol
30	5.71	62.1	104	1.92	7.41	4.83	1	—	0.704	0.467	Aq. alcohol
31	—	—	7.19	—	—	2.55	1	—	—	0.917	"
32	—	—	—	—	—	1.50	1	—	—	—	"
33	8.00	7.53	9.80	1.99	—	2.02	1	—	—	0.709	"
35 (0.554)	—	5.61	6.67	0.513	—	1.91	1	0.054	0.797	0.660	Water
37	—	—	—	—	—	4.03	1	—	—	0.518	Alcohol
38	1.90	—	10.0	—	—	1.53	1	—	—	0.64	isoPropyl alcohol
Group B.											
1	5.73	0.906	0.625	2.93	1.79	1.20	1	1.46	(1.56)	26.5	40% Acetic acid
2	0.0936	0.191	0.161	0.163	0.369	0.375	1	—	—	(1.66)	"
3	0.084	0.090	0.074	0.35	0.24	0.62	1	4.84	1.39	10.53	Aq. alcohol
4	0.134	0.182	0.184	0.392	0.300	0.830	1	3.24	1.15	4.15	"
8	—	0.064	—	—	—	0.50	1	—	—	3.00	Benzene
11	—	—	—	0.0095	0.045	0.42	1	2.86	2.06	18.76	Alcohol
15	0.000455	0.00264	0.00623	—	—	—	1	2.73	2.91	0.114	Water
17	0.099	0.167	0.122	0.136	0.196	0.173	1	0.189	1.21	2.09	Alcohol
19	0.0366	0.156	0.0635	0.507	0.493	0.527	1	1.10	1.25	1.36	"
20	0.0466	0.203	0.100	0.668	0.573	0.560	1	1.04	1.11	1.35	"
21	—	—	—	0.476	0.396	0.560	1	1.03	1.15	1.31	"
36	—	—	—	1.21	0.63	1.06	1	2.89	1.11	2.26	Water
Group C.											
9	1.77	6.93	11.5	1.46	1.46	0.85	1	Large	1.46	2.89	Aq. acetone
10	—	—	—	1.09	1.33	1.95	1	2.53	1.12	1.58	Alcohol
24	0.0654	0.692	0.610	—	—	—	1	0.259	1.10	0.563	"
25	0.050	0.559	0.673	—	—	—	1	—	—	—	"
34	0.0258	0.940	1.13	0.153	—	0.959	1	0.105	0.928	0.844	Water

## References.

- (1) and (2) *N*-Chlorination re-calculated from Table I.
- (3) Hydrolysis of benzyl chlorides at 83°. Olivier *et al.*, *Rec. trav. chim.*, 1922—1926.
- (4) Reciprocals of times of half completion of hydrolysis of benzyl bromides at 76° and 60°. Lapworth, Shoosmith, *et al.*, *J.*, 1922—1926.
- (5) Same data for reduction of benzyl bromides by HI at 101° and 25°; refs. as (4).
- (6) and (7) Hydrolysis of benzenesulphonyl chlorides at 25° in 1:1 acetone-water and alcohol-water respectively, Berger and Olivier, *Rec. trav. chim.*, 1927, 46, 516.
- (8) Friedel-Crafts reaction with same compounds, *Rec. trav. chim.*, 1914, 33, 244; 1927, 46, 605.
- (9) Hydrolysis of benzoyl chlorides at 0°. Berger and Olivier, *loc. cit.*
- (10) Benzyl chlorides and sodium ethoxide at 30°, Franzen and Rosenberg, *J. pr. Chem.*, 1921, 101, 335.
- (11) *k*<sub>1</sub> for diphenylchloromethanes and ethyl alcohol at 25°, Norris, *Z. physikal. Chem.*, 1927, 130, 662.
- (12) Same for benzoyl chlorides at 0°.
- (13) *k*<sub>2</sub> for hydrolysis of formamides by NaOH at 100°, Davis, *J.*, 1909, 95, 1397; *Z. physikal. Chem.*, 1912, 78, 353, 369.
- (14) Same data for acetanilides.
- (15) Decomposition of diazo-compounds, Cain and Nicoll, *J.*, 1902, 81, 1412; 1903, 83, 206.
- (16) Diazotisation of anilines at 0°, Boeseken, Brandama, and Schoutinsen, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, 23, 249; compare Tassilly, *Bull. Soc. chim.*, 1920, 27, 19.
- (17) Anilines and 1-chloro-2:4-dinitrobenzene at 7°, change % after 15 hrs., Linke, *Ber.*, 1923, 56, 348.
- (18) Saponification of phenylsuccinimides at 25°, Sanna, *Gazzetta*, 1927, 57, 761; —OH<sub>2</sub> results not directly comparable, Micolatti and Longo, *Atti R. Accad. Lincei*, 1896, 1, 351.
- (19) *k*<sub>1</sub> for sodium phenoxides and ethylene oxide at 70.4°, Boyd *et al.*, *J.*, 1914, 105, 2117; 1919, 115, 1239.
- (20) Same data for propylene oxide.
- (21) Modified *k*<sub>2</sub> for sodium phenoxides and ethyl iodide at 42.5°, Goldsworthy, *J.*, 1926, 1254.
- (22) Phenols and acetic anhydride at 100° (Panoff, A., 1903, ii, 357), in non-polar medium (benzene). Figures only for —CH<sub>3</sub>. Not quoted in table.
- (23) Benzoylation of phenols; all results not directly comparable and not included in table; Bernoulli and Gosar, *Helv. Chim. Acta*, 1926, 9, 780; compare van Duin, *Rec. trav. chim.*, 1927, 46, 189.
- (24) Esterification by 2% HCl at 25°, Goldschmidt, *Ber.*, 1895, 23, 3218.

- (25) Esterification in alcohol with 0.3333*M*-HCl and 0.05*M*-water, Kallan, *Monatsh.*, 1906—1907; *Annalen*, 1907, **351**, 186.  
 (26) Esterification in absence of added catalyst at 135°, % change after 5 hrs., Michael *et al.*, *Ber.*, 1909, **42**, 310, 317.  
 (27) Saponification of methyl benzoates at 25°; % changed after 2 hrs.  
 (28) Same after 65 mins., Kellas, *Z. physikal. Chem.*, 1897, **24**, 221.  
 (29) Saponification of ethyl benzoates at 30°, McCombie and Scarborough, *J.*, 1915, **107**, 156.  
 (30) Hydrolysis of ethyl benzoates by NaOH at 30°, Kindler, *Annalen*, 1926, **450**, 1; 1927, **452**, 90; 1928, **464**, 278. Figures also for compounds of types (31) Ar-CH<sub>2</sub>-CO<sub>2</sub>Et, (32) Ar-CH<sub>2</sub>-CH<sub>2</sub>-CO<sub>2</sub>Et, (33) Ar-CH=CH-CO<sub>2</sub>Et.  
 (34) and (35) Hydrolysis of benzamides by HCl and baryta respectively, Reid, *Amer. Chem. J.*, 1899, **21**, 284; 1900, **24**, 397.  
 (36) Reduction of phenylhydrazines by stannous chloride and HCl, Franzen, *J. pr. Chem.*, 1918, **97**, 61.  
 (37) Addition of hydrogen sulphide to nitriles at 60-6° and 1.75 atm. with NaSH as catalyst. Ref. as (30).  
 (38) Benzoyl chlorides and isopropyl alcohol at 25°; ref. as (12) and also Norris and Gregory, *J. Amer. Chem. Soc.*, 1928, **50**, 1813.

the table that the effect of chlorine is in almost all reactions in the same sense as that of the nitro-group, its inductive influence thus predominating. Analysis of the superposed alternating effects shows that here the results are complex. It may be noted that there is little evidence in Table II for the occurrence of "steric hindrance" due to a single ortho-substituent, though there are indications in reactions in which a carbonyl group is involved (24—35; compare Olivier, *Rec. trav. chim.*, 1929, **48**, 227). Another instance is recorded by Pfeiffer, Engelhardt, and Alfuss (*Annalen*, 1928, **467**, 158) in the esterification of benzonitriles.

In considering, now, the place to be taken by the results of Table I, we see that *N*-chlorination of acetobenzylamides falls unequivocally into Group B. With acetanilides, the results are more complex. When the acetamido-group is directly attached to the nucleus it can act as a strong *op*-directing group, and, in fact, with acetanilide, *N*-chlorination comprises less than 1% of the total reaction. The allocation of *N*-chlorination to Group B of Table II suggests that it is a reaction which is facilitated by flux of electrons towards the nitrogen, so that *N*- and *C*-chlorination are competing processes. Factors tending to obstruct the sharing of electrons between the nitrogen atom and the nucleus will assist *N*- as against *C*-chlorination; thus acetobenzylamide is *N*-chlorinated twice as fast as acetanilide, and *C*-chlorinated at a negligible rate. The results show that in the acetanilides, the introduction of chlorine atoms into the nucleus also reduces the preponderance of *C*-chlorination, an effect only partially offset in *m*-chloroacetanilide by the mutual reinforcement of the *op*-directing activities of the two groups. Indeed, in the acetanilides, chlorine in all positions accelerates *N*-chlorination. This may be ascribed in the *o*- and *p*-compounds to a dominant tautomeric influence by the halogen atom, but the result with the *m*-compound is unexpectedly high. At the same time, chlorine retards the reaction with the acetobenzylamides in all positions without alternation, the inductive effect of the halogen atom presumably dominating the situation,

owing to the methylene group's intervening between the nitrogen atom and the nucleus. The nitro-group depresses reactivity in both series, but, somewhat unexpectedly, far more effectively in the acetobenzylamides than in the acetanilides. The high value for *o*-nitroacetanilide is unexpected, as is also the extraordinarily high rate of reaction of aceto-*p*-toluidide. The *p*-methyl group produces no such effect in the acetobenzylamides, but it may be noted that it has marked effects in reactions 3, 11, and 15 of Table II. There seems to be no analogy in Table II for the special effect of the *o*-nitro-group, unless it be in reaction 35, where it appears to upset the normal reaction completely. (For "ortho-effects," compare also van Duin, *Rec. trav. chim.*, 1927, 46, 256; Kindler, *Annalen*, 1928, 464, 278.)

The view that *N*-chlorination is a reaction favoured by factors tending to produce a crowding of electrons at the nitrogen atom is supported by the fact that the rates for acetamide, aceto- $\beta$ -phenylethylamide, acetobenzylamide, and acetanilide lie in a continuous decreasing series; for the phenyl group acts as an "electron sink" towards the nitrogen atom, since (a) these substances are chlorinated or nitrated in positions *op*- to the nitrogen atoms, and (b) the approach of the phenyl group towards the nitrogen atom lowers the basic properties. Since *N*-chlorination cannot proceed by the separation of an anion, it seems probable that the vital stage is the attraction of the positive component of an incipiently ionised chlorine molecule, much as in the process of nuclear chlorination.

*Nuclear Chlorination.*—Table I contains two new results for nuclear chlorination—those for *m*-chloroacetanilide, mentioned above, and for aceto-*m*-toluidide. The latter, as we should expect, is *C*-chlorinated far more rapidly than acetanilide. On the other hand, the high rate of *C*-chlorination of the para-isomeride is another unexpected effect of the *p*-methyl group. This effect has been observed before, as is shown by Table III, which gives the relative values of  $k_c$  in glacial acetic acid (Orton and King, *loc. cit.*), in 40% acetic acid, and also in water (Soper, 1927, *loc. cit.*). The figures in parentheses are the values of  $k_N/k_c$ .

TABLE III.

Medium.	Acetanilide.		<i>o</i> -Cl.	<i>p</i> -Cl.	<i>o</i> -CH <sub>3</sub> .	<i>p</i> -CH <sub>3</sub> .
	Abs.	Rel.				
Glacial acetic ...	40	1	0.0018	0.0053	0.23	1.93
40% Acetic ...	11,000	1 (0.0087)	0.0025 (10.4)	0.0123 (0.85)	0.126 (0.101)	1.68 (0.137)
Water .....	17,000	1 (0.0076)	0.0026 (13.6)	0.0124 (0.91)	—	—

*Limitations of Solvents.*—It is to be noted in Table III that a parallelism in the values of  $k_c$  exists in spite of the change in medium,

and also despite the intrusion of simultaneous *N*-chlorination in the aqueous media. The change in solvent is, however, comparatively slight, and it should also be observed that in all the reactions in Table II, *the solvents are very similar*, only one being non-polar. This fact limits the generality of the conclusions to be drawn from the experiments. The results shown in Tables I and II are based upon experiments in which a standard substance is made to react with a series of compounds having various substituents inserted at positions remote from the point of reaction; a connexion is then traced between the changes in the reaction rate and the influence supposed to be exerted by the inserted groups upon the bond actually concerned in the reaction (*e.g.*, compare Norris, *Z. physikal. Chem.*, 1927, **130**, 662; Norris *et al.*, *J. Amer. Chem. Soc.*, 1925—1929). The electronic theory permits clearer definition since it ascribes the effects of substituents to their varying "electron affinities," which modify electronic configurations at the reacting atom, and external physical evidence (*e.g.*, from electric moments) is sometimes available as to the quality of the electron affinities. Consequently the process is now sometimes inverted, and the mechanism of a reaction is inferred from the effects of substituents on its speed (see above, also *Ann. Reports*, 1927, 1928). But these comparative experiments are usually made with solutions, wherein reaction velocity is notoriously susceptible to the influence of environment, the action of which may be *specific* to each reacting substance (Christiansen, *Z. physikal. Chem.*, 1924, **113**, 35; McCombie, Scarborough, and Smith, J., 1927, 802; Norrish and Smith, J., 1928, 129; Richardson and Soper, J., 1929, 1873). Hence, although identical conditions of solvent, vessel, and temperature are employed, so that the only variable is the constitution of one reactant, yet, owing to variations of environmental influences with constitution, the resulting series of reaction rates may fail to register the effects of substituents upon the point of reaction in the molecule. Little information is available on the effect of changing the medium upon comparative rates of reaction of a series of compounds with a standard substance, but this view is supported by the fact that changes of solvent alter the order of the relative rates of reaction of benzyl chloride and its nitro-derivatives with trimethylamine (McCombie, Scarborough, and Smith, *loc. cit.*), and similar effects were observed in other reactions by Berger (*Rec. trav. chim.*, 1927, **46**, 856), by Menshutkin (*Z. physikal. Chem.*, 1900, **34**, 157), and by Blakey, McCombie, and Scarborough (J., 1928, 2863).

On the other hand, it may happen that for a series of related substances, the effects of environment are sufficiently similar to justify drawing the desired inferences connecting the reaction rates

directly with the influence of constitution upon reactivity (see Bradfield and Jones, J., 1928, 1006, 3073; also Hückel, *Ber.*, 1928, 61, 1517; 1929, 62, 2040). Bearing in mind this possibility, together with (a) the inevitable variation in precision in the different measurements quoted in Table II, and (b) the possibility of unsuspected wall effects in certain cases (Bailey, J., 1928, 1204), the general measure of consistency observed in Table II suggests that the only positive conclusion which can be drawn from the available data is that comparative velocity measurements can be used as indications of the effects of substituents upon the point of reaction in the molecule when an assembly of reactions can be examined. Individual anomalies in particular reactions (such as those observed in *N*-chlorination) may be genuine effects of the substituent upon the position of attack in the molecule, or may, at least in part, be due to the imperfect separation of environmental factors as indicated in the foregoing discussion.

#### EXPERIMENTAL.

*Materials.*—Acetanilides were prepared by acetylation of purified anilines, and repeatedly recrystallised from alcohol or dilute acetic acid. Aceto- $\beta$ -phenylethylamide (from the amine) and acetamide were purified by two distillations at 0.5 mm. Benzylamine and its monochloro- and mononitro-substituted derivatives were made (as hydrochlorides) from the corresponding benzyl chlorides by the method of Ing and Manske (J., 1926, 2348), *m*-chlorobenzyl chloride being prepared by chlorination of *m*-chlorotoluene at its boiling point (Kenner and Witham, J., 1921, 119, 1460). The acetobenzylamides were obtained by acetylation of the benzylamine hydrochlorides by warming with excess of acetic anhydride and sodium acetate. In each case, the excess of acetic anhydride was hydrolysed with water, the solution made alkaline with potassium hydroxide, and the (partly precipitated) acetyl derivative extracted with chloroform and recrystallised several times, usually from alcohol or hot water. The following compounds could not be traced in the literature: Aceto-*p*-chlorobenzylamide, m. p. 109.5°, after crystallisation from hot water until of constant m. p. (Found: Cl, 19.1.  $C_9H_{10}ONCl$  requires Cl, 19.3%); aceto-*m*-chlorobenzylamide, m. p. 38°, purified by distillation at 0.5 mm. (Found: Cl, 19.0%). The low m. p. of the *m*-compound as compared with its isomerides is in accord with the rule for disubstituted benzenes (*Ann. Reports*, 1926, 144). (I am indebted to Messrs. W. O. Jones, B.Sc., and G. I. Davies, B.Sc., for the analyses.)

*p*-Methylbenzylamine was made by reducing *p*-toluonitrile with sodium and alcohol; and the other materials required—reaction



medium, chlorine, etc.—were prepared as described by Orton, Soper, and Williams (*loc. cit.*).

*Velocity Measurements.*—The experimental method employed, the precautions taken, and the control experiments applied were those described previously, alternate portions of the reaction mixture being analysed at known time intervals (*a*) for chlorine by titration with *N*/500-sodium thiosulphate, and (*b*) for chloroamine by removal of chlorine with saturated aqueous *p*-cresol and subsequent titration. The initial concentrations of chlorine and of anilide were of the order 0.0005—0.0010*M* and 0.001—0.005*M* respectively, and, as before, hydrochloric acid was always present in 0.01*M* concentration in order to suppress the hydrolysis of chlorine. In view of the more strongly basic character of the acetobenzylamides as compared with the acetanilides, it was considered advisable to test the effect of hydrogen chloride upon the rate of *N*-chlorination. With 0.01*M*-, 0.05*M*-, and 0.10*M*-hydrochloric acid present, the values of  $k_N$  for acetobenzylamide were respectively 170, 176, and 173, showing that there is no appreciable effect over this range of concentration. The heat of reaction was shown to be negligible.\*

The velocity coefficients were calculated as before from the equations for a bimolecular reaction following two courses simultaneously. The following experiment is typical of the results with benzylamides.

*Expt. 133.* Aceto-*m*-nitrobenzylamide = 0.004109*M*; chlorine = 0.001232*M*; HCl = 0.01*M*; thiosulphate = 0.949  $\times$  *N*/500.

Time (mins.)	0	1.10	3.10	5.00	5.90	8.10	10.20	13.40	15.10
Titre (c.c.) ...	1.44	11.98	4.81	11.90	6.80	11.75	8.62	11.62	9.72

From curves constructed with these figures, we have :

Time.	KI titre.	:NCl titre.	Diff.	Change, %.	$k$ .
0	12.08	1.44	10.64	18.0	—
1.00	12.03	2.73	9.30	28.3	35.3
3.10	11.93	4.81	7.12	45.1	35.0
5.90	11.83	6.80	5.03	61.2	35.4
10.20	11.71	8.62	3.09	76.1	35.2
13.40	11.62	9.38	2.24	82.8	34.5

Mean 35.1

Corrected value for  $k_N$  = 33.5.

In experiments such as the above, in which the fall in potassium iodide titre is slight and may be due partly or wholly to accidental loss of chlorine, no reliance can be placed on the result for  $k_C$ ;  $k_N$  is corrected for the fall of potassium iodide titre. Two methods of calculation are possible, on the assumptions (*a*) that the fall is due entirely to *C*-chlorination; (*b*) that it is due entirely to accidental loss, in which case there is no corresponding consumption of anilide. As, however, the anilide is always present in large excess,

the two methods give results which do not differ greatly: in the above experiment,  $k_N$  as calculated by method (b) lies between 32.9 and 34.4. Method (a) has been used throughout, since *C*-chlorination does actually take place slowly with some of the anilides in question (unpublished work by Dr. B. Jones).

The results in parentheses in Table I are provisional only. That for aceto-*m*-toluidide is the mean of five experiments in which potassium iodide was added to the whole of the reaction mixture at a noted time, less than 0.1 min. after mixing. A trial of the method with acetanilide gave a result  $k_C = 10,400$  compared with the previous value 11,000. The ratio  $k_N/k_C$  was found by a separate experiment (see Orton, Soper, and Williams, *loc. cit.*; method for acetanilide). The value given for acetamide is the mean of three concordant experiments, but certain other experiments suggest that complications may arise in the reaction with this substance. The figure for aceto-*p*-methylbenzylamide is the mean of two experiments only and awaits confirmation.

Measurements were also made with 2:4-dinitroacetanilide. One experiment is shown below. Zero time was about 1 min. after mixing.

*Expt.* 145. 2:4-Dinitroacetanilide = 0.001542*M*; chlorine = 0.000623*M*; HCl = 0.011*M*; thiosulphate =  $0.972 \times N/500$ .

Time (mins.)	0	1.00	1.85	2.75	3.80	4.70	6.40	7.50
Titre (c.c.)	6.30*	2.75	2.86	2.61	6.09*	2.87	2.76	5.81*

The titres marked \* were those with potassium iodide alone; *p*-cresol was used with the others. *N*-Chlorination evidently takes place rapidly until the chloroamine concentration reaches a certain value, after which its titre remains constant, although there is still a large amount of free chlorine left. Moreover, the final chloroamine titre was lowered by increasing the initial hydrogen chloride concentration. It thus appears that the chloroamine equilibrium (Orton and Jones, J., 1909, 95, 1456),  $C_6H_5(NO_2)_2 \cdot NHAc + Cl_2 \rightleftharpoons C_6H_5(NO_2)_2 \cdot NClAc + HCl$ , lies much further to the left in 40% acetic acid than with the other anilides examined. This observation with 2:4-dinitroacetanilide is in accord with the fact recorded by Soper and Smith (J., 1928, 138) that the introduction of a single nitro-group into the benzene nucleus greatly increases the hydrolysis constant of a chloroamine.

I wish to express my sincerest thanks to Professor K. J. P. Orton, F.R.S., and to Dr. F. G. Soper for their most valuable advice and help. It is a pleasure, also, to acknowledge the assistance I have received by discussion with Dr. A. E. Bradfield.

X.—*The Dehydration of Copper Sulphate Pentahydrate.*

By WILLIAM E. GARNER and M. G. TANNER.

MEASUREMENTS of the rates of evaporation of water vapour from salt hydrates have usually been made by placing crystals of the hydrate in an atmosphere of air over a suitable dehydrating agent (compare Rae, J., 1916, 109, 1229; Crowther and Coutts, *Proc. Roy. Soc.*, 1924, 106, 215). Under such conditions, an induction period is frequently observed, due to the slow rate at which centres of dehydration are formed on the surface (Langmuir, *J. Amer. Chem. Soc.*, 1916, 38, 2263). In such cases, the maximum rate of evaporation is not attained until the crystals have undergone considerable decomposition. Removal of the air increases the rate of evaporation, but the induction period is not thereby removed (compare Bružs, *Z. physikal. Chem.*, 1929, B, 3, 434).

The haphazard formation of centres of dehydration on the surfaces of crystals leads to the formation of curved surfaces of evaporation, the areas of which, after a given time, are dependent on the number of centres formed, their position, and their time of origin. The area of the interface from which the water is liberated is thus dependent on chance, and is so uneven that it can neither be measured accurately nor evaluated.

These difficulties can be avoided by employing large single crystals of known area which have been activated by rubbing with the product of the dehydration. For example, a crystal of the pentahydrate of copper sulphate, after being rubbed with the monohydrate and placed in a vacuum, forms innumerable centres all over its surface, and the interface which is ultimately formed between the pentahydrate and the monohydrate consists of a series of planes running parallel to the original surfaces of the crystal. This makes it easy to determine the area of the interface from the dimensions of the crystal and the weight of water which has been lost at any time from the beginning of the dehydration. Thus, values for the rate of evaporation from unit area of interface can be calculated.

For an absolute measurement of rate of evaporation, it is clear that the water molecules must evaporate into a space from which return to the surface is impossible. Such an arrangement cannot readily be obtained in practice, but the rate of return can be made very small by using high vacua and suitably shaped containing vessels. An experimental arrangement is described below, which, as a result of many trials, has been found to be satisfactory for this purpose.

From the temperature coefficient of the rate of evaporation, the

critical increment of the process of evaporation can be obtained. The significance of this energy is uncertain, unless the unit process to which it refers is known. There will be at least three possible rates to take into account—(1) the rate of loss of water at the interface  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ – $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$ , where  $x$  may be 3, 1, or 0, (2) the rate of diffusion of water vapour across the layer of dehydrated substance, which increases in thickness with time, and (3) the rate of evaporation of water from the external surface of the crystal. If (1) is the rate which determines the velocity of evaporation, then  $v/A$ , where  $v$  is the velocity and  $A$  the area of the interface at any time, will be constant throughout the whole process; if (2) is important, then  $v/A$  should decrease as the crystal is dehydrated; and if (3) corresponds to the process measured, then the velocity of evaporation will be independent of the time. Experiment shows that  $v/A$  does not change very markedly with the thickness of the dehydrated layer, so that in the case of the pentahydrate of copper sulphate, the slowest process is the change occurring at the interface between the unchanged and the dehydrated substance.

#### EXPERIMENTAL.

Crystals of the pentahydrate of copper sulphate weighing 0.2–0.5 g. were employed. These were grown slowly from small crystals at room temperature, and during growth, were turned over frequently. In the selection of these crystals, attention was paid to their freedom from defects, and those with numerous facets were rejected. Their thickness was measured by a micrometer screw gauge, and the other dimensions were measured by means of a Zeiss glass scale calibrated in 0.5 mm. The surfaces of these crystals were activated by 15 minutes' rubbing with copper sulphate monohydrate enmeshed in a piece of silk.

The crystals of copper sulphate were suspended singly in the apparatus described below by means of four thin pieces of platinum wire attached to a quartz-fibre spring made after the manner of McBain (*J. Amer. Chem. Soc.*, 1926, 48, 690).<sup>\*</sup> The quartz springs, made by winding on a steel rod, were calibrated by measuring the elongation under known weights, a Wilson travelling microscope being used for this purpose.

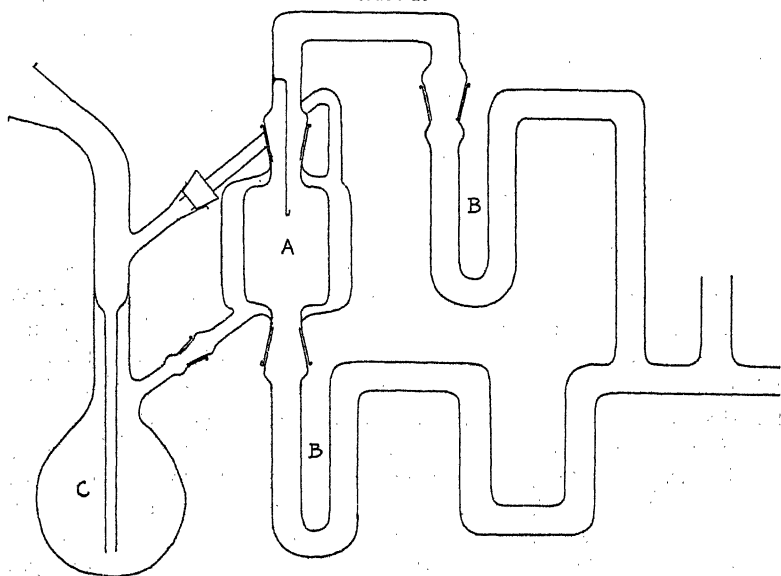
*Apparatus.*—Several forms of apparatus were tried, in all of which the water was removed in a high vacuum by pumping the vapour through U-tubes immersed in liquid air. In the earlier forms, the water was pumped off below the crystal by one exit (Apparatus A),

<sup>\*</sup> This balance has been used by Hume and Colvin in a study of the decomposition of potassium hydrogen oxalate hemihydrate (*Proc. Roy. Soc.*, 1929, A, 125, 642).

but in the later types, in order to prevent the return of water molecules to the crystal from above, it was removed by two exits, one above and the other below the crystal (apparatus C; see Fig. 1). The bulb containing the crystal was placed in a constant-temperature oven in the earlier experiments, and surrounded by the vapour from a constant-boiling liquid in the later experiments.

In Fig. 1, A is a Pyrex vessel, 5 cm. in diameter and 15 cm. long, in which the crystal is suspended. It was surrounded by the vapour from C or else by water at a constant temperature. The water vapour was withdrawn through wide tubing 2 cm. in diameter, and *via* the two U-tubes B immersed in liquid air.

FIG. 1.



A Hyvac pump and a mercury condensation pump were used in evacuation, and the pressures read on a McLeod gauge. The rates of evaporation were affected when there was a small leak of air into the apparatus, but no effect was observed if the pressure was kept lower than  $10^{-4}$  cm.

The dehydrated crystals were found to consist of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  unless the experiment was unduly prolonged. The rate of loss of water from the monohydrate is very slow: even at  $80^\circ$ , a crystal originally weighing 0.339 g. (see Expt. I) lost only 0.00093 g. per hour after it had been converted into monohydrate.

Partly dehydrated crystals show a core of unchanged hydrate, and the surfaces of this core run parallel to the surfaces of the

original crystal. The thicknesses of the dehydrated substance,  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , were practically the same on all faces.\* This simplified the calculation of the change in the area of the interface with time.

*Area of Interface.*—The boundaries of the areas of the faces of the crystal and of the area of its chief cross-section were first drawn on squared paper. On the same diagrams were drawn the boundaries of the faces and cross-section of the core of pentahydrate which remained at various stages in the dehydration: the stages chosen were those corresponding to definite thicknesses of the shell of monohydrate. From these diagrams, the areas of the interface and the volumes of the core for four stages in the process of dehydration were evaluated. This treatment gave the volume of unchanged pentahydrate and the area of interface for each of four values of the thickness of the shell of changed salt. The loss of water and the related values, the changes in length of the quartz spring corresponding to the areas of interface so calculated, are readily obtained from the volumes. The values of the area of interface were then plotted against decrease in length of the quartz spring.

#### *Experimental Results.*

The decrease in the length of spring depends on the weight of the crystal and the sensitivity of the spring; on an average, it was about 0.6 cm. Such a change could be measured to about 1 part in 600 parts. The dehydration was in general followed until the pentahydrate was completely converted into the monohydrate; beyond this point, loss of water was very slow, and the crystal became dark. The decrease in length of spring, calculated from the original weight of the crystal, assuming that dehydration proceeds to monohydrate, was in two cases 0.602 and 0.374 cm. The observed values were 0.604 and 0.370 cm., respectively. Typical curves of length of spring plotted against time are given in Fig. 2. The curve for  $56^\circ$  (Curve II) is curious in that, when 2 mols. of water had been lost, there was a marked decrease in the rate of evaporation (see later).

The following results (Expts. I and II) were obtained with an early form of the apparatus in which water was removed by one exit only. The tables give the dimensions of the crystals, the time in hours,† the decrease in length of the spring ( $x$ ), the change in length of spring *per hour* ( $dx/dt$ ), the area of the interface,  $A$ , and the velocity of dehydration,  $k$ , expressed as g. of water lost *per*

\* These were measured by breaking a partly dehydrated crystal and examining the depth of penetration under the microscope. These depths were the same within 10%.

† The first of the times given for each experiment includes that required to heat the crystal to the temperature of the experiment, and hence has little significance.

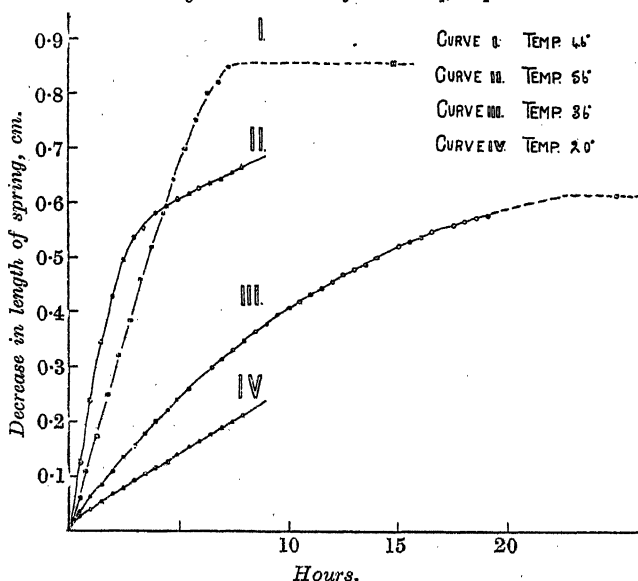
minute from unit area of interface. The total elongation given is the change in length of spring at the end of the dehydration to  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ .

Expt. I. Temp. =  $36.5^\circ$ ; weight = 0.339 g.; area of crystal =  $2.40 \text{ cm}^2$ ; thickness = 0.205 cm.; sensitivity of spring = 6.15 cm./g.; total elongation = 0.60 cm.

$t$ .....	0.75	1.8	2.8	4.0	5.2	6.6	9.7	13.8
$x$ , cm. ....	0.05	0.10	0.15	0.20	0.25	0.30	0.40	0.50
$dx/dt$ .....	0.050	0.048	0.046	0.042	0.038	0.036	0.030	0.023
$A$ , $\text{cm}^2$ .....	2.32	2.29	2.20	2.11	2.00	1.85	1.52	1.13
$k \times 10^5$ ...	5.8	5.7	5.7	5.4	5.2	5.3	5.3	5.5

FIG. 2.

Dehydration curves for  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .



The loss of water was measured up to a composition of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , at which the rate of evaporation decreased abruptly to about 0.0002 g. per hour. The extrapolated value for  $k$  at zero time is  $5.8 \times 10^{-5}$ , and its value is practically constant throughout.

Expt. II. Temp. =  $36.5^\circ$ ; weight = 0.216 g.; area of crystal =  $1.96 \text{ cm}^2$ ; thickness = 0.144 cm.; sensitivity = 6.15 cm./g.; total elongation = 0.35 cm.

$t$ .....	1.0	2.2	3.5	5.1	6.9	9.2
$x$ , cm. ....	0.05	0.10	0.15	0.20	0.25	0.30
$dx/dt$ .....	0.044	0.040	0.036	0.030	0.023	0.0175
$A$ , $\text{cm}^2$ .....	1.85	1.72	1.60	1.40	1.25	1.00
$k \times 10^5$ .....	6.4	6.3	6.1	5.4	5.0	4.8

In Expt. II, the crystal was smaller than that in Expt. I, and it had a greater ratio of area to volume. The values of  $k$  decreased with time from  $6.4$  to  $4.8 \times 10^{-5}$  g./min. Similar decreases occurred in Expts. III and IV, and a drift is also observable in Expt. VII.

*Apparatus B.*—The results given in Expt. III were obtained with an apparatus similar to that shown in Fig. 1, except that the constant temperature was obtained by placing the apparatus in an air thermostat. The water was removed both above and below the crystal, without, however, changing the magnitude of  $k$  appreciably.

Expt. III. Temp. =  $36.5^\circ$ ; weight =  $0.282$  g.; area of crystal =  $2.33$  cm.<sup>2</sup>; thickness =  $0.150$  cm.; sensitivity =  $6.91$  cm./g.; total elongation =  $0.57$  cm.

$t$ .....	1.6	3.1	5.2	7.6	9.2	10.8
$x$ , cm. ....	0.1	0.2	0.3	0.4	0.45	0.50
$dx/dt$ .....	0.063	0.054	0.046	0.036	0.030	0.024
$A$ , cm. <sup>2</sup> .....	2.22	2.00	1.74	1.48	1.30	1.10
$k \times 10^5$ .....	6.8	6.5	6.4	5.9	5.6	5.3

*Apparatus C.*—A further change was then made in which the dehydration chamber was jacketed and the crystal maintained at constant temperature by the vapour of boiling ether.

Expt. IV. Temp. =  $35.1^\circ$ ; weight =  $0.479$  g.; area of crystal =  $3.10$  cm.<sup>2</sup>; thickness =  $0.190$  cm.; sensitivity =  $6.91$  cm./g.; total elongation =  $0.95$  cm.

$t$ .....	1.25	2.5	4.1	5.8	7.7	9.9	12.4	15.4
$x$ , cm. ....	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80
$dx/dt$ .....	0.076	0.070	0.062	0.055	0.049	0.042	0.037	0.033
$A$ , cm. <sup>2</sup> .....	3.00	2.85	2.7	2.52	2.32	2.15	1.95	1.75
$k \times 10^5$ .....	6.1	5.9	5.5	5.3	5.1	4.7	4.6	4.6

Expt. V. Temp. =  $35.1^\circ$ ; weight =  $0.205$  g.; area of crystal =  $1.86$  cm.<sup>2</sup>; thickness =  $0.1135$  cm.; sensitivity =  $10.52$  cm./g.; total elongation =  $0.60$  cm.

$t$ .....	1.4	3.1	5.0	7.2
$x$ , cm. ....	0.1	0.2	0.3	0.4
$dx/dt$ .....	0.060	0.057	0.050	0.0425
$A$ , cm. <sup>2</sup> .....	1.75	1.60	1.47	1.35
$k \times 10^5$ .....	5.5	5.7	5.4	5.3

Expt. IV shows a very appreciable fall in the values of  $k$ . In the calculation of the critical increment, it will therefore be necessary to use the value for the velocity coefficient obtained by extrapolation back to zero time. In Expt. V, with a much smaller crystal, the rates per unit area are practically constant.

*Experiments in the Neighbourhood of Room Temperature.*—At this temperature, the rate of evaporation is so slow that the dehydration



was not followed up to the monohydrate stage, so that there is not so large a drift in the values of  $k$ .

Expt. VI. Temp. =  $26.5^{\circ}$ ; weight = 0.266 g.; area of crystal =  $2.10 \text{ cm.}^2$ ; thickness = 0.134 cm.; sensitivity = 6.91 cm./g.

$t$ .....	1.1	2.8	4.6	6.6	8.6	10.8
$x$ , cm. ....	0.05	0.10	0.15	0.20	0.25	0.30
$dx/dt$ .....	0.030	0.027	0.027	0.025	0.0245	0.0205
$A$ , cm. <sup>2</sup> .....	2.05	2.00	1.90	1.84	1.73	1.62
$k \times 10^5$ .....	3.5	3.3	3.5	3.3	3.4	3.1

Expt. VII. Temp. =  $21.5^{\circ}$ ; weight = 0.348 g.; area of crystal =  $2.31 \text{ cm.}^2$ ; thickness = 0.156 cm.; sensitivity = 10.52 cm./g.

$t$ .....	1.5	2.0	2.5	3.5	4.0	6.5	8.0
$x$ , cm. ....	0.068	0.084	0.103	0.140	0.153	0.230	0.270
$dx/dt$ .....	0.040	0.037	0.035	0.034	0.031	0.030	0.028
$A$ , cm. <sup>2</sup> .....	2.22	2.20	2.16	2.10	2.07	1.98	1.94
$k \times 10^5$ ...	2.9	2.7	2.6	2.6	2.4	2.4	2.3

Expt. VIII. Temp. =  $20.5^{\circ}$ ; weight = 0.202 g.; area of crystal =  $1.75 \text{ cm.}^2$ ; thickness = 0.106 cm.; sensitivity = 10.52 cm./g.

$t$ .....	2.20	3.25	5.25	7.30
$x$ , cm. ....	0.075	0.10	0.15	0.20
$dx/dt$ .....	0.0265	0.0245	0.0245	0.024
$A$ , cm. <sup>2</sup> .....	1.67	1.65	1.60	1.55
$k \times 10^5$ .....	2.5	2.35	2.4	2.45

*Results at the Temperature of Boiling Carbon Disulphide,  $46^{\circ}$ .—* Expts. IX, X, and XI were carried out at  $46^{\circ}$ . On account of the rapidity of the change, no measurements could be made of the rate in the very early stages of the dehydration. At this temperature, the values of  $k$  do not decrease with time in the manner found with some of the experiments at  $36^{\circ}$ . There was, however, evidence of an induction period. Only the early part of Expt. XI was satisfactory.

Expt. IX. Temp. =  $46.25^{\circ}$ ; weight = 0.263 g.; area of crystal =  $2.49 \text{ cm.}^2$ ; thickness = 0.111 cm.; sensitivity = 10.52 cm./g.; total elongation = 0.85 cm.

$t$ .....	1.08	1.78	2.8	3.6	4.8	5.7
$x$ , cm. ....	0.15	0.25	0.40	0.50	0.65	0.75
$dx/dt$ .....	0.140	0.149	0.138	0.123	0.119	0.102
$A$ , cm. <sup>2</sup> .....	2.30	2.17	1.97	1.80	1.64	1.42
$k \times 10^5$ .....	9.7	11.0	11.1	10.8	11.5	11.3

Expt. X. Temp. =  $46.0^{\circ}$ ; weight = 0.325 g.; area of crystal =  $2.41 \text{ cm.}^2$ ; thickness = 0.152 cm.; sensitivity = 10.52 cm./g.; total elongation = 0.99 cm.

$t$ .....	2.4	3.25	4.1	5.1	6.1	7.2	8.4	9.0
$x$ , cm. ....	0.25	0.35	0.45	0.55	0.65	0.75	0.85	0.90
$dx/dt$ .....	0.117	0.114	0.109	0.102	0.093	0.087	0.085	0.071
$A$ , cm. <sup>2</sup> .....	2.12	2.00	1.86	1.70	1.60	1.45	1.30	1.12
$k \times 10^5$ ...	8.9	9.1	9.4	9.6	9.2	9.5	10.3	10.0

Expt. XI. Temp. =  $45.7^{\circ}$ ; weight = 0.282 g.; area of crystal =  $2.31 \text{ cm.}^2$ ; thickness = 0.143 cm.; sensitivity = 10.52 cm./g.

$t$ .....	1.0	2.5	3.5
$x$ , cm. ....	0.118	0.307	0.417
$dx/dt$ .....	0.125	0.121	0.101
$A$ , $\text{cm.}^2$ .....	2.14	1.91	1.79
$k \times 10^5$ .....	9.3	9.9	9.0

*Results at the Temperature of Boiling Acetone,  $56^{\circ}$ .*—At this temperature also, the dehydration proceeds at a constant rate per unit area of interface, but there is a curious difference between the dehydration at this temperature and that at lower temperatures (see Fig. 2). A break occurs on the dehydration curve at the composition  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , and if the crystal is broken at this stage, there is no core of pentahydrate. The interface thus moves into the crystal at a relatively faster rate than is the case for experiments at lower temperatures, since only 2 mols. of water are lost instead of 4. The dehydration of  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  proceeds slowly, and after partial dehydration to  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , the crystal shows a more amorphous structure than when it has been dehydrated to  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  directly. In the latter case, the pseudomorph breaks along the old cleavage planes of the crystal, but crystals dehydrated at  $56^{\circ}$  do not show this feature when broken.

Expt. XII. Temp. =  $56.0^{\circ}$ ; weight = 0.423 g.; area of crystal =  $2.57 \text{ cm.}^2$ ; thickness = 0.180 cm.; sensitivity = 10.52 cm./g.; elongation at break = 0.65 cm.

$t$ .....	1.0	1.45	1.95	2.55
$x$ , cm. ....	0.25	0.35	0.45	0.55
$dx/dt$ .....	0.236	0.231	0.183	0.163
$A$ , $\text{cm.}^2$ .....	2.12	1.85	1.64	1.40
$k \times 10^5$ .....	17.7	19.8	17.8	18.4

Expt. XIII. Temp. =  $55.85^{\circ}$ ; weight = 0.325 g.; area of crystal =  $2.31 \text{ cm.}^2$ ; thickness = 0.145 cm.; sensitivity = 10.52 cm./g.; elongation at break = 0.48 cm.

$t$ .....	0.75	1.25	1.75
$x$ , cm. ....	0.180	0.290	0.390
$dx/dt$ .....	0.226	0.208	0.174
$A$ , $\text{cm.}^2$ .....	2.00	1.75	1.49
$k \times 10^5$ .....	18.0	18.9	18.5

Expt. XIV. Temp. =  $56^{\circ}$ ; weight = 0.249 g.; area of crystal =  $2.26 \text{ cm.}^2$ ; thickness = 0.206 cm.; sensitivity = 10.52 cm./g.; elongation at break = 0.56 cm.

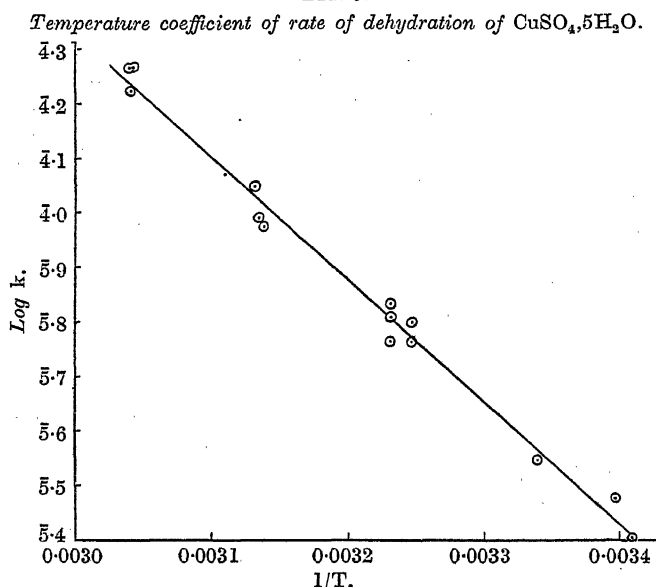
$t$ .....	1.0	2.0	2.5	3.0
$x$ , cm. ....	0.252	0.392	0.460	0.518
$dx/dt$ .....	0.180	0.133	0.126	0.103
$A$ , $\text{cm.}^2$ .....	1.77	1.36	1.16	0.93
$k \times 10^5$ .....	16.1	15.5	17.3	17.6

The dehydration of  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  occurs at the following rates : For Expt. XII, 0.0022 g./hour; for XIII, 0.0019 g./hour; and for XIV, 0.0021 g./hour.

*Temperature Coefficient of the Dehydration.*—The following table gives the rates of evaporation per unit area. Where the rates show a drift, the value for zero time has been taken, but where there is evidence of an induction period, this has been ignored in the evaluation of  $k$ .

Temp. ....	20.5°	21.5°	26.5°	35.1°	36.5°	46.0°	56.0°
$k \times 10^5$ ...	2.55	3.0	3.5	5.8	5.8	9.4	16.8
				6.3	6.4	9.7	18.4
					6.8	11.1	18.4

FIG. 3.



The values of  $\log k$  are plotted against the reciprocal of absolute temperature ( $1/T$ ) in Fig. 3, and the values at 56.0° lie on the same straight line as those for the other temperatures. The value for the critical increment is 10,300 \* calories, and the value of  $\mu$  calculated from this is 2.77, which corresponds to one of the vibration frequencies of the water molecule.

#### Discussion.

Any detailed discussion of the results can have but little value until further hydrates have been studied. The main features which

\* This critical increment is very much smaller than that found by Topley and Hume (*Proc. Roy. Soc.*, 1928, A, 120, 211) for the decomposition of  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ .

are of interest may, however, be examined. It is rather surprising that the rate of evaporation is so little affected by the thickness of the dehydrated salt. Experiment shows that there is a constant unidirectional streaming of molecules from unit area of the interface  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ – $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  to the surface of the crystal. The structure of the material through which the molecules escape can only be guessed. Its nearest analogue is probably that of the structure of amorphous carbon. The molecules probably escape through capillary passages, the diameter of which is of the same order as that of the molecular diameter of water. Thus the movement occurs within the range of the attractive forces of the molecules forming the capillaries, and will thus correspond to that which occurs in an adsorbed gas film. There will be a pressure gradient in the adsorbed film which lies between the interface and the surface of the crystal. This is necessarily the case, since the molecules after leaving the interface expand from regions of small to regions of greater volume. The rate of return of water molecules to the interface will depend on the pressure exerted by the water molecules at the interface, just as in the case of a three-dimensional system, and this rate will be negligible only if the pressure in the neighbourhood of the interface is negligible. It is unlikely that this is the case when the interface is covered by a layer of dehydrated substance, so that the constancy of the values of  $k$  may mean that the pressure in the neighbourhood of the interface is constant at constant temperature and independent of the thickness of layer of dehydrated salt. Thus the values of  $k$  so far obtained may not be the true rates, and hence the temperature coefficient may not give the true critical increment of the dehydration process. Evidence for this view must be sought in measurements of the rate of evaporation in the very early stages of the dehydration of the crystal, when the dehydrated layer is thin, and such measurements can be accurately made only at low temperatures. The curves obtained for  $20^\circ$  (compare curve IV, Fig. 2) are practically linear, but if the linear portion of the curves be extrapolated back to  $t = 0$ , they do not pass through the origin. The rate of dehydration over the first hour is much larger than the steady rate reached subsequently.

The change in the nature of the dehydration phenomena which occurs between  $46^\circ$  and  $56^\circ$  also provides an indication that the constant rates are not true rates. At  $56^\circ$  the dehydration product is the trihydrate, whereas at  $46^\circ$  it is the monohydrate. This behaviour can be explained in terms of the pressure of the water molecules in the surface gas film of the dehydrated layers. As the temperature rises, this pressure increases until it may become greater than the equilibrium pressure of water over the trihydrate.

Since at  $56^{\circ}$ , this hydrate is not dehydrated until the whole of the pentahydrate has disappeared, it is evident that the surface pressures in the dehydrated layers must be greater than the dissociation pressure of the trihydrate. If such pressures prevail, then the possibility of return of water molecules to the interface is always present.

The slow rates of dehydration of the monohydrate and the trihydrate are also of interest. The trihydrate on dehydration does not give a visible interface similar to that obtained when the pentahydrate is dehydrated. Evaporation appears to proceed from the whole of the internal surface of the pseudomorph. The movement of the water molecules may therefore be restricted by the production of discontinuities in the internal surface of the dehydrated substance.

#### *Summary.*

The rates of dehydration of single crystals of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  have been measured in a vacuum over a range of temperatures from  $20^{\circ}$  to  $56^{\circ}$ . Crystals of known weight and area were activated by rubbing with the powder of the monohydrate. Such crystals after partial dehydration gave a core of pentahydrate, the surfaces of which ran parallel to the original surfaces of the crystal. The rate of loss of water divided by the area of the interface between the pentahydrate and the dehydrated product was practically constant for the higher temperatures, but in some experiments at the lower temperatures, the velocity coefficient decreased as dehydration proceeded.

Below  $46^{\circ}$  the dehydrated product was the monohydrate, which remains in the form of a pseudomorph which loses water very slowly. At  $56^{\circ}$ , the first product of the dehydration is the trihydrate, which does not decompose until all of the pentahydrate has disappeared. The trihydrate then slowly gives up its water at a constant rate.

A straight line is obtained by plotting  $\log k$  against the reciprocal of the absolute temperature,  $k$  being the velocity coefficient per unit area of interface. The critical increment of the process is 10,300 calories, and  $\mu = 2.77$ , which corresponds to one of the vibration frequencies of the water molecule.

It is concluded that the rates measured may not be the true rates of evaporation, and that the critical increment may not be the true value for the unit process which occurs at the interface.

Our thanks are due to Imperial Chemical Industries Ltd. for a grant for the purchase of apparatus.

## XI.—*Low-temperature Oxidation. Part II. The Ignition of Some Hydrocarbons in Oxygen.*

By JOHN STANLEY LEWIS.

It is now generally recognised that paraffin hydrocarbons react readily with oxygen at comparatively low temperatures. The temperatures at which rapid oxidation sets in during the slow heating of mixtures of hydrocarbons and oxygen in glass bulbs have been investigated by the author, and some of the conditions noted (J., 1927, 1555; 1929, 759). In the pressure-temperature curves, peculiar increases of pressure occurred at points termed "critical inflexion temperatures" (*C.I.T.*). The slope of the curve above the point of inflexion was influenced by factors such as the rate of heating and the concentration of oxygen and hydrocarbon. This is accounted for by a variation in the velocity of the reactions; increase in concentration caused a more rapid rise in pressure, but on the other hand, a faster rate of heating permitted less time for chemical action to proceed.

The above experiments in slow heating of oxygen-hydrocarbon mixtures occasionally resulted in explosions, and since these occurred at temperatures near the *C.I.T.*, it was surmised that the chemical actions pertaining to the *C.I.T.* were closely connected with explosion or self-ignition temperatures of these mixtures, the main difference being one of velocity. The following work is an investigation of this relationship.

The various methods in use for the measurement of ignition temperatures give discordant results to such an extent that it has become necessary to introduce the qualifying term "relative ignition temperatures" (Mason and Wheeler, J., 1922, 121, 2079), for comparable values can only be obtained when important governing factors (*e.g.*, material and surface area of the igniting vessel, volume of the chamber, concentration of reacting gases, pressure, etc.) are maintained constant. The current methods can be classified as (*a*) crucible method, (*b*) dynamic tube method, (*c*) bomb method, and (*d*) adiabatic compression of the mixture. The gradual heating of mixtures until explosion occurs does not appear to have been described. It is not suggested that the following method, though simple in design, can supersede any of the foregoing methods, but the results help to illustrate many well-established facts connected with ignition temperatures and the difficulties of obtaining even relative values.

## EXPERIMENTAL.

The apparatus consisted simply of a cylindrical bulb (of 125 or 225 c.c. capacity) of good soda glass fitted with a piece of glass tubing  $3\frac{1}{2}$ " long, the end of which was corrugated to enable a piece of rubber pressure tubing 4" long to be firmly attached; the open end of the latter was closed by a stout clip before the mixture in the bulb was heated. The bulb was cleaned with chromic acid and water and dried in a hot air oven by a current of dry air. In an experiment, the cooled bulb was filled with oxygen, and the desired quantity of hydrocarbon was introduced in a small tube drawn off at one end to a sealed capillary, the rubber tubing then being closed with the clip. The capillary was broken when required by shaking the bulb. For experiments of a comparative nature, it is sufficient to measure out the hydrocarbon with a capillary pipette. A bulb of specified dimensions, and filled at atmospheric pressure, being used in a series of experiments, the mass of oxygen remains practically constant.

The conditions requisite for the exploding of the hydrocarbon-oxygen mixtures by progressive heating are (a) sufficiently rapid rise in temperature, (b) adequate concentration of oxygen, and (c) a concentration of hydrocarbon above a certain minimum. At the temperature of explosion the rubber tubing is burst, and occasionally the bulb itself is shattered. The bulbs were therefore enclosed in a copper-gauze cage, and the observer was protected by a plate-glass shield. The explosion temperature is governed by many factors, of which the following have been studied.

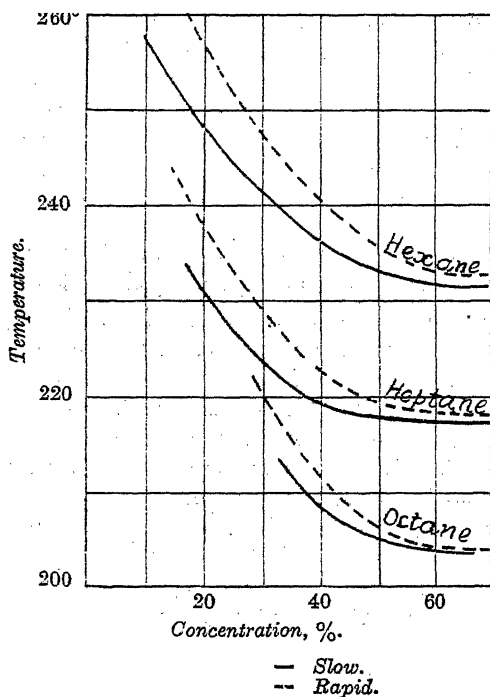
*Concentration.*—Other conditions remaining constant, an increase in concentration of a paraffin hydrocarbon tends to lower the explosion temperature until a minimum is obtained. For dilute mixtures, results were only reproducible to within  $3^{\circ}$  or  $4^{\circ}$  owing to difficulty in adjusting the rate of heating, and as a mean of a large number of experiments the curves in Fig. 1 were drawn; the minimum temperature, however, is correct to within  $1^{\circ}$ . The curves exhibit certain points of interest.

(a) For a particular rate of heating, a minimum concentration is necessary to obtain an explosive action, and more dilute mixtures will not explode. This minimum increases rapidly with rise of molecular weight in the case of paraffins. Thus, with a 225 c.c. bulb and a rate of heating of just under  $1^{\circ}$  per min., concentrations of hexane below 10% failed to explode, but extensive oxidation had occurred, as revealed by analysis and by the fact that when the experiment was repeated with a mercury manometer attachment, the pressure-temperature curve showed a well-defined *C.I.T.* at

234—235°. Therefore, it is assumed that, although rapid oxidation had set in at this temperature, the conditions were not such as to give rise to ignition. For octane a concentration of at least 33% was necessary for explosion, whereas all concentrations of *isodecane* (*diisooamyl*) failed to ignite unless a greater rate of heating was employed.

The foregoing affords a rough measure of the ease of oxidation of these hydrocarbons, and, in general, it seems that the minimum

FIG. 1.



percentage for ignition by this method increases with the instability towards oxygen. This applies also to unsaturated hydrocarbons, which will not explode except at high concentrations and rapid rates of heating, the hexylene minimum being much higher than that for amylene.

(b) The character of the explosion is controlled by the concentration of the original mixture. With rich mixtures a minimum explosion temperature obtains, but in the case of paraffin hydrocarbons the explosion is a mild one with a low note, often an absence of flame, and no carbon deposit—just sufficient pressure has been



suddenly generated to burst the rubber tubing. The residual gases in the bulb contain traces of carbon monoxide and dioxide, and the liquid condensed on the walls gives aldehydic reactions. It must be emphasised that the mixture is well outside the usual explosive range of hydrocarbons and in the neighbourhood of equimolecular concentrations. With a reduction in the hydrocarbon content, the violence of the explosion seems to increase until a maximum is reached when the ratio approaches that necessary for complete combustion. In such cases the explosions were sufficiently intense at times to shatter the glass bulb and were always accompanied by flame.

(c) The fall of the curves to the minimum is not without significance. The lighter members of the series are more resistant to, or react more slowly with, oxygen; they can be heated well above the minimum ignition temperature, especially in dilute mixtures, and are less liable to pre-ignition in internal-combustion engines.

*Rate of Heating.*—A more rapid rate of heating tends to raise the ignition temperature. The chemical reactions occurring at the C.I.T. are comparatively slow, and in the case of dilute mixtures may be insufficient to give rise to explosion. It will therefore be a simple matter to "superheat," as it were, the mixture to a temperature above the ignition point obtained by a slower rate of heating, thereby accelerating the chemical action and causing an explosion which is far more violent than with the slower speed. An increase in the hydrocarbon ratio has an opposing effect because it increases the velocity of the reaction and tends to lower the explosion point. It will therefore be more difficult to "superheat" rich mixtures above the ignition temperature. These facts are illustrated in Fig. 1, where the variations of ignition temperatures are given for two widely different rates of heating and for various concentrations.

The olefins, however, do not show this great rise of ignition temperature with speed of heating, and, moreover, because they are more readily oxidised, their minimum concentration for ignition is much higher than that of the corresponding paraffin. Thus, for all conditions tried with amylene, the explosion temperatures only varied between  $240^{\circ}$  and  $244^{\circ}$ , but even with rich mixtures violent explosions were obtained.

A combination of the two factors already mentioned, *viz.*, a high concentration of hydrocarbon and a slow rate of heating, must tend towards a minimum explosion temperature. These minima can be taken as relative ignition temperatures for many of the hydrocarbons, and Table I contains some results obtained by this method. They are of interest in that they are much lower than the ignition temperatures recorded in the literature, which have been obtained by

other methods, and also because they approximate to the *C.I.T.*'s of these hydrocarbons.

TABLE I.

Hydrocarbon.	Minimum ignition temp.	<i>C.I.T.</i>
<i>n</i> -Pentane .....	255—257°	255°
<i>n</i> -Hexane .....	232—233	230
<i>n</i> -Heptane .....	218—220	209
<i>n</i> -Octane .....	203—204	197
<i>iso</i> Decane (Diisoamyl) .....	210	—
Amylene .....	241—242	240
Trimethylethylene .....	243—244	—
Methylethylethylene .....	251—252	—
Hexylene .....	229—230	—

The lowest ignition temperature obtained for *isodecane* (210°) is higher than that of octane (204°). In order to bring about the explosion of *isodecane*, which is very readily oxidised at 200°, it is essential that a high concentration be used and a rapid rate of heating, about 4—5° per min., otherwise the experiment fails. A strict comparison, therefore, can only be made where equimolecular concentrations are subjected to the same rate of heating. Two bulbs containing octane and *isodecane* of about equal concentrations were very rapidly heated in the same bath with sufficient speed to explode them: the former ignited at 217° and the latter at 211°.

Presumably there is no distinction between the *C.I.T.* of a mixture and the explosion temperature, except one of degree. The curves of Brunner and Rideal (J., 1928, 1162) for hexane-oxygen, maintained at constant temperatures below the *C.I.T.*, terminate in a rapid rise in pressure. An examination of the curves (*a*), (*b*), and (*c*) (*ibid.*, p. 1166) reveals the fact that the slope at the *C.I.T.* is more inclined to the vertical, and the angle with the vertical increases with the lowering of temperature. This is as one would expect, since the chemical changes involved decrease in velocity with lowered temperature. It might be reasoned that these changes can be accelerated by concentration, and thus explosive reactions might be obtained below the *C.I.T.* by keeping the gases at a constant temperature. A 50% hexane mixture in a 225 c.c. bulb was maintained at a temperature just below the *C.I.T.* At 228° an explosion resulted, but lower temperatures failed to cause ignition. A weaker mixture, with 35% hexane and immersed in the same bath, also failed to explode. It may happen that the 50% mixture would explode at a still lower temperature if initially compressed, but it is not possible to attempt this in glass bulbs.

*Catalytic Actions.*—Many investigations have been carried out upon the influence of surface and of positive and negative catalysts on ignition temperatures, but the results are frequently conflicting.

In comparison with metallic surfaces, it is usually stated that glass and silica surfaces have a very low activity on the oxidation of hydrocarbons, so that the result with a plain glass surface will be taken as a zero. This problem of catalytic action is so complex that the following experiments must be regarded as qualitative and introductory. The oxidation of these hydrocarbons proceeds in stages, and it is clear from what follows that the course of the reactions and the nature of the final products are dependent on the surface in contact with the reacting gases.

(a) *Powdered glass.* The ignition point of paraffins is raised in all cases, the amount depending on the rate of heating and the concentration, but variation in the weight of glass between 0.2 and 1.0 g. had little effect. In one set of experiments, the ignition point of octane was raised from 204° to 218° and that of hexane from 232° to 257°, but the differences diminish greatly with rich mixtures and slower temperature rise. On the other hand, the ignition temperature of amylene underwent little change in the presence of powdered glass, but the violence of the explosion was considerably decreased. Powdered pumice behaves similarly.

(b) *Charcoal.* The action of this catalyst is noteworthy in that it affects paraffins and olefins in opposite directions, and the extent varies with the nature of the charcoal. The ignition temperature of paraffins was *raised*, whilst that of amylene was *lowered considerably*; with wood charcoal (0.5 g.) which has been powdered, sieved (60 mesh), and strongly heated in a covered crucible, and with the same rate of heating, 40% mixtures of the various hydrocarbons gave the following results :

Hydrocarbon .....	$C_8H_{18}$	$C_7H_{16}$	$C_6H_{14}$	$C_5H_{10}$
Blank expt. ....	205°	220°	233°	240°
Charcoal present .....	220	249	254	210

Amylene appears to vary more widely with different charcoals, and explosions at 200°, 210°, and 227° were obtained with three samples. Decolorising charcoal failed to cause an explosion under any conditions of concentration and rate of heating, although the hydrocarbon was considerably oxidised.

(c) *Metals.* Metals may have no effect on the ignition point, or may raise the temperature or even inhibit explosion in some instances, according to the metal employed, extent and condition of the surface, concentration of hydrocarbon, and the speed of heating.

(i) *Silver.* In one set of experiments the silver was deposited on the inside of the bulb, and in another set a strip of the metal was enclosed. The explosion temperatures were raised considerably in every case; thus, octane gave 204° (blank), 212° (silver coating), and 214° (silver strip).

(ii) Platinum. The results were much as those for silver. Octane gave 205° (blank), 218° (strip), and 212° (coating), whilst hexane gave 232° (blank) and 249° (strip).

(iii) Tin, Zinc, and Aluminium. There was no appreciable rise in explosion temperatures with  $4'' \times \frac{1}{8}''$  strips of metal with freshly cleaned surfaces. All hydrocarbons in the presence of any one of them detonated within 0—2° of the blank. The metallic surfaces remained bright, and light yellow liquids condensed in the bulb on cooling.

(iv) Lead. The temperature of ignition is considerably raised and explosion may even be inhibited. A  $4'' \times \frac{1}{8}''$  strip of the metal was heated with 50% octane-oxygen at a rate of about 2° per min. No ignition occurred up to 275°, and examination of the bulb after cooling showed that the surface of the metal had been attacked, yielding a loose greyish powder easily rubbed off; a dark brown viscous gum collected on the bottom of the bulb, but the walls remained clear. When opened under water, the bulb became about three-quarters filled with liquid, and qualitative examination denoted the presence of carbon dioxide and monoxide, a trace of oxygen, and a small remainder of combustible gases that burned with a non-luminous flame.

(v) Copper. This metal also prevented the ignition of octane, but the appearance of the bulb was very different from that in which lead had been heated. A brownish skin was deposited over the whole surface of the glass, and the copper was only tarnished if it had not had a preliminary cleaning, but was blackened by a film of oxide if the surface had been freshly scraped. Opening the bulb under water gave a residue of gas appreciably more than in the experiments with lead, but it was qualitatively similar.

The effect of these two metals diminishes with decrease in molecular weight of the hydrocarbon, and the ignition temperature of pentane was raised only 2° and that of hexane 7° by approximately the same sized strips of metal.

(vi) Iron. A 50% octane mixture was slowly heated with a strip of steel: a violent explosion occurred at 207°, shattering the glass bulb. This was the first instance of such an event with this hydrocarbon, for under all other conditions the bulb remained intact. The surface of the steel remained bright.

The results obtained in the foregoing experiments may be discounted because the metals are coated with oxide films at the temperature of explosions. As will be suggested later, the lag is a far more satisfactory measurement than the ignition temperature, and experiments are now in progress on the effect of metal surfaces and metallic oxides on the time of lag.

(d) *Lead tetraethyl*. The minimum explosion temperature was raised in every case, sometimes as much as  $40^{\circ}$ , depending on the concentration of lead tetraethyl (up to a maximum effect), the rate of heating, and the surface area of the glass in contact with the gases. The last factor was illustrated by heating 50% hexane-oxygen mixtures in a bulb with various proportions of powdered glass and lead tetraethyl, the rate of heating being the same in each experiment. In presence of 1 g. of powdered glass, the ignition temperature with a 0.9% lead tetraethyl solution in hexane was  $260^{\circ}$ , and for 0.2 g. of the glass it was  $274^{\circ}$ . Again, a 0.25% solution of the lead compound raised the ignition temperature of hexane to  $269^{\circ}$  in the presence of 0.1 g. of powdered glass, but only to  $240^{\circ}$  with 1.0 g. It is apparent that the ratio of lead tetraethyl to powdered glass is a controlling factor in the rise of ignition temperature, the latter tending to inhibit the action of the lead compound.

The effect of increasing concentration of lead tetraethyl on the explosion temperature of octane is shown in the following results.

PbEt <sub>4</sub> , % .....	0	1	2	3	4	5
Explosion temp. ....	$204^{\circ}$	$230^{\circ}$	$232^{\circ}$	$238^{\circ}$	$239^{\circ}$	$238^{\circ}$

*Volume of Bulb*.—Two bulbs of 125 c.c. and 225 c.c. capacity were filled with oxygen-hydrocarbon mixtures of as nearly as possible the same composition. They were connected by a piece of pressure tubing and heated in the same bath to about  $160^{\circ}$ , so that equalisation of pressure (and possibly also of concentration) was effected; they were then separated by clamping the tubing at two points and cutting the rubber between the clamps. Both bulbs exploded within a few seconds of each other on further heating.

*Concentration of Oxygen*.—It is usually stated that the ignition temperature as determined by the usual method is lower in oxygen than in air, but it must be stressed that other variables are introduced: when determinations are made with air, the oxygen, on account of its lower concentration, may be consumed before explosion is possible; with pure oxygen, a higher concentration of hydrocarbon can be introduced, thereby reducing the explosion temperature to a minimum. When air was substituted for oxygen in the glass bulbs, the hydrocarbons could not be ignited by rapid heating in a bath, although this can be done when the rate of heating is much greater, as in the crucible methods, etc., or when the mixture is suddenly heated in a tube or bomb initially at a high temperature. An atmosphere of 50% oxygen-nitrogen failed to ignite a given weight of hexane heated at a rate of  $3^{\circ}$  per min., whereas with 75% oxygen content in the bulb originally, explosion took place at  $247^{\circ}$ . On repeating the latter experiment and comparing it with a bulb

containing pure oxygen and the same weight of hexane as a check, the latter exploded at 245°. Many such experiments with paraffins indicated that increase in oxygen content tends to lower the ignition temperature, but the effect is small compared with that of the hydrocarbon. Amylene, however, showed practically no change of ignition temperature when exploded in various concentrations of oxygen. The presence of nitrogen in the lowered concentrations may have some effect, but this has not been investigated. By making a fine slit in the rubber tubing attached to the bulbs, the pressure inside is maintained at atmospheric pressure, but the concentration of both reactants is diminished, and this would be expected to raise the ignition temperature. This was found to be the case, except that a more rapid heating is necessary to cause explosion; thus, hexane exploded at 256°. These results were more comparable with those obtained by the crucible method, and some experiments of the latter kind were carried out in test tubes, the effect of the same factors being investigated.

*Test-tube Experiments.*—*Air.* The tubes were almost wholly immersed in an oil-bath at the required temperature, and drops of the liquid were allowed to fall into them from a capillary tube, the quantity being varied until lowest ignition was obtained. Experiments with *closed* and *open* mouths proved that the former gave much lower ignition temperatures with air and oxygen. Thus, in a 7" × 1" test-tube the minimum ignition temperature in air for octane was 225–226°, and 214° when a tightly fitting lid was applied—the mouth of the test-tube was ground down to a level surface and the lid smeared with plasticine to make it air-tight. Various numbers of drops of octane were introduced at decreasing temperatures until no signs of ignition or rapid oxidation occurred. Between each trial the residual gases in the tube were blown out and any signs of carbon deposit removed. Ether was found to ignite at 183–184° by such a method in a 7" × 1" tube. For the final tests, it is essential that freshly cleaned tubes be used each time in order to obtain the lowest ignition point.

These experiments are noteworthy since they emphasise the facts that there is no line of demarcation between the rapid oxidation temperature and the ignition point, and that the time of lag can be much longer than is generally supposed. At temperatures well above the ignition point, the lag is comparatively short, and the flame and characteristic sound of explosion well defined, but as the temperature is lowered these become less definite and the time for their appearance much longer. By using the covered-tube method, the author obtained lags of over 500 secs. on many occasions with rich mixtures of hydrocarbons dropped into oxygen. Under such

conditions no explosion sound can be heard, but a slight puff which pushes up the lid slowly, and furthermore, there is no apparent flame.

The diameter of the test tube is also an important factor, although beyond 7" the length had no appreciable effect. With the 7" tubes, the ignition point was at first lowered with increased diameter but was subsequently raised with still wider tubes, although the concentration of hydrocarbon was increased proportionately, thus :

Diameter.	Ignition temp. in air for	
	octane.	hexane.
0.75	221°	271°
1.00	214	265
1.25	216	268
1.50	219	269

*Oxygen.* Ignition temperatures in oxygen are lower than in air; thus, for a 7"  $\times$  1" tube, the following results were obtained.

Hydrocarbon .....	$C_5H_{12}$	$C_6H_{14}$	$C_7H_{16}$	$C_8H_{18}$	$C_9H_{20}$
Temp. in air .....	305°	265°	247°	214°	—
„ oxygen .....	295°	248°	235°	207°	270°

*Powdered glass and pumice.* The ignition temperature is raised, depending on the weight of powder, up to a maximum on the molecular weight of the hydrocarbon (or, more correctly, its ease of oxidation). Thus, the increase for the same weight of pumice is more for octane than for hexane.

*Charcoal.* The temperature of paraffin hydrocarbon ignition in oxygen is raised; thus in 7"  $\times$  1" tubes, 0.2 g. of charcoal required a temperature of 221° to ignite octane and 254° for hexane. Amylene exploded in oxygen alone at 270°, but at 268° in the presence of charcoal. The concentration of amylene required to bring about explosion is always much higher than that of paraffins.

*Metals.* These may be classified as (a) those having little effect, such as aluminium, tin, and zinc (see above), and (b) those promoting oxidation and raising the ignition temperature, such as platinum, copper, and lead, the effect being greater the lower the molecular weight. Interesting results were obtained with a copper test-tube 6"  $\times$  1", the inner surface of which had been cleaned and polished. The ignition temperature of octane in air was 223° at first, but after repeated experiments the readings were much higher, and even in oxygen the hydrocarbon would not ignite at 225° after such treatment. It is evident that deposits interfere with successive results, and the surface must be renewed for each experiment. When this was done, the original value of 223° was obtained.

*Lead tetraethyl.* As in the previous experiments, the temperature of ignition was raised in all cases, e.g., hexane in air to 283° by a

1% concentration of the lead compound, the lag being nearly 300 seconds. The addition of powdered glass or pumice reduces the ignition temperatures and the lag. The latter at 278° was 250 secs. for 0.2 g. of powdered pumice, but ignitions were obtained as low as 273° with 1.0 g. of pumice.

### *Discussion.*

Mason and Wheeler (*loc. cit.*) have pointed out that when such mixtures as have been used in the foregoing experiments are gradually heated, the rate of combination of oxygen and hydrocarbon increases; and so the heat evolved by the reaction raises the temperature of the products and unburnt gases above that of the external source of heat. There will be a tendency for the rate of reaction to increase until the whole of the hydrocarbon or oxygen is consumed. When, however, the initial temperature imparted to the walls of the vessel is sufficiently high, the rate of reaction will become so rapid as to produce flame. This statement is only partially true, and the above observations apply to experiments in which oxygen-methane mixtures were allowed to enter an evacuated silica bulb maintained at a comparatively high temperature, so that the mixture is heated much more rapidly than in the present experiments. The heat of the reaction at this high temperature cannot be dissipated as quickly and will undoubtedly be utilised in raising the temperature of the contained gases and hence the velocity of their reaction, which will become explosive. It is incorrect, however, to state that oxygen-hydrocarbon mixtures react with gradually increasing velocity with rise of temperature as suggested above, because the author (*loc. cit.*) has shown that there is a definite transition from slow chemical action to rapid action at a temperature which has been termed the *C.I.T.*, and Brunner and Rideal (*loc. cit.*) have proved that for hexane-oxygen mixtures this rapid change may take place at still lower temperatures when the mixtures are maintained at constant temperatures for lengthy intervals. The transition from very slow oxidation to explosion is still far more abrupt when anti-oxidants are added, such as lead tetraethyl, which reduces the reaction considerably almost up to the temperature of explosion. Moreover, neither the "lag" interval nor the catalytic effects of promoters and inhibitors of oxidation receive a satisfactory explanation from the above statement.

In order to account for such facts as the last, the theory of chain mechanism has recently been applied to the combustion of hydrocarbons, notably by Egerton and Gates (*J. Inst. Pet. Tech.*, 1927, 281; *Nature*, 1928, 121, 10) and also by Brunner and Rideal for hexane (*loc. cit.*). The latter workers have measured the amounts



of peroxides or "moloxydes" of hexane during the period of autoxidation, but the author believes that these peroxides are produced from the unsaturated hydrocarbon initially formed by primary dehydrogenation (see Part I; J., 1929, 759). Further, the fall in pressure noted by these authors for hexane-oxygen at 210° is not definitely proved to be a measure of the moloxyde formation. Similar experiments have been repeated with silica and glass bulbs and the pressure drop in the former is appreciably less, indicating greater surface action with glass. The amount of gummy residue was larger in the glass bulb, and this would suggest that the fall in pressure is chiefly due to the formation of condensation products. In the case of unsaturated hydrocarbons, this fall of pressure is much more pronounced (see Part I) and leads to the conclusion that the chemical change involved is the same, although the velocity differs, being much greater for amylene. The primary dehydrogenation would therefore be a comparatively slow reaction, especially at first (see Part I), and probably takes place in the gaseous phase. This would account, in part at least, for the fact that metallic lead has no inhibiting action whilst lead tetraethyl vapour is particularly effective at this stage of the oxidation, if one could assume (in spite of some adverse opinions) that the vapour of lead resulting from the decomposition of the tetraethyl is the active component. It is also significant that this anti-oxygen does not inhibit the oxidation of amylene to the same extent as that of pentane.

The successive stages in the combustion of paraffin hydrocarbons suggested by the author are: (a) primary dehydrogenation resulting in unsaturated hydrocarbons, (b) combination of the latter with oxygen to produce unstable peroxides, (c) decomposition of the peroxides *per se* to aldehydes, etc., which are further oxidised to water and oxides of carbon if the mixtures are rich in oxygen. The velocities of these step reactions probably vary widely in themselves and still more so in the presence of catalysts. According to the chain-reaction mechanism, then, when hydrocarbon-oxygen mixtures are slowly heated, as in the experiments of the author and of Brunner and Rideal, or during the "lag" interval present in the determination of auto-ignition temperatures, there will be an increase every moment of the active centres present due to one cause or another, and after a certain lapse of time, which may extend to several minutes as shown in the experimental part (autoxidation), they may be present in such concentration as to give rise to rapid pressure increase without flame or even to explosion. The reaction is exothermic, and when approximately equimolecular concentrations are used, the products are chiefly aldehydic, acid, or gummy, with very small proportions of the oxides of carbon and water. If there

is present a large excess of oxygen, the oxidation becomes far more violent and complete, owing to the liberation of heat in this initial reaction, which raises the temperature of the whole system and brings about the further oxidation of the peroxide decomposition products.

An increase in concentration of hydrocarbon tends to reduce the auto-ignition temperature (see Mason and Wheeler, J., 1924, 125, 1869), whereas the oxygen concentration produces a much smaller effect. These authors attribute this phenomenon to the fact that the component with the greater "stopping power" for radiant energy such as will "activate" it, increases the rate of reaction with the concentration. Or, according to the chain mechanism, the increase of hydrocarbon molecules is said to augment the number of chains formed in unit time and hence the number of active centres. The oxygen concentration lowers the ignition to a much smaller extent, as pointed out above. Moore (*J. Inst. Pet. Tech.*, 1919, 186) added 70% of carbon dioxide to the oxygen, and, using a platinum crucible method, found an inappreciable difference in the ignition temperature of kerosene. White and Price (J., 1919, 115, 1462) and Mason and Wheeler (*loc. cit.*), using two different methods, obtained appreciable changes with variations in the air/fuel ratio; they did not actually study the effect of oxygen concentration, since the mass of fuel was not maintained constant. The auto-ignition temperature, then, is a function of the concentration of hydrocarbon and, to a much smaller extent, of oxygen. If either or both of these are consumed during the pre-flame period, no ignition obtains. Insufficient active centres have been produced, or, in other words, the accumulation of peroxides has been too slow and one or the other of the reactants has disappeared before ignition occurs. Hence it will be necessary to raise the temperature of the mixture of similar composition in order to accelerate the formation of active centres in unit time, i.e., the autoxidation, and thus produce an explosion. The lag has been decreased. It should follow from the above view that the ignition temperature of a given mixture will be lowered by an increase in pressure, but very little work has been done on this subject. There is a possibility that the effect of increased concentration by pressure would be nullified at a lower temperature by the reduction in the rate of formation of reactive centres, so much so that these would be deactivated before explosion could occur; this would to a certain extent reduce the effect of increased pressure.

The effect on the ignition temperature of various materials has received much consideration but results are at variance (Moore; White and Price, *loc. cit.*; Egerton and Gates, *J. Inst. Pet. Tech.*,

1927, 244); for paraffin hydrocarbons, however, the author proves that some metals, such as aluminium, tin, nickel, and zinc, have little if any effect upon the explosion temperature, whereas others, such as silver, iron, platinum, copper, and lead, raise the temperature of ignition and may even prevent the explosion. It is suggested that this is brought about by the removal of the peroxides on the surface of these metals, yielding aldehydes or their polymerised products (gums), the exact nature of the decomposition being determined by the temperature and the nature of the metal employed. An increase in the number of chains broken in unit time may be said to have been taking place on the metallic surfaces. The same result is brought about by an increase in the surface of the glass in contact with the gas, which will account for the rise in explosion temperature occasioned by the presence of powdered glass and pumice, or the etching of the internal surface of the vessel. The action of carbon on the paraffins and olefins is noteworthy. Towards the former it acts similarly to powdered glass and pumice in raising the ignition point. The powdered charcoal is a strong absorbent; it is also reputed to be a destroyer of peroxides, and since these are readily formed by olefins, the rate of oxidation and the heat evolution may be so rapid as to give rise to local ignition, which will account for the low ignition point of amylene at a charcoal surface.

In the glass-bulb experiments, the difference in the ignition temperatures with change of volume from 125 c.c. of 225 c.c. was inappreciable probably owing to the high concentrations of oxygen and hydrocarbon. In closed glass tubes of various diameters, White and Price (*loc. cit.*) found that the temperature decreased at first and then increased with increasing diameter of the tube. The test-tube method indicated a similar result, but it is apparent that when narrow test-tubes are used the initial concentration of the reactants will be small and one or the other will be consumed before the desired concentration of active centres is attained.

The results with lead tetraethyl confirm those of Egerton and Gates (*J. Inst. Pet. Tech.*, 1927, 244) and of Weerman (*ibid.*, p. 300), but if, as the former point out, anti-knocks do influence the ignition temperatures, it will not follow that the converse is true, *viz.*, that substances which raise the ignition temperatures of a fuel are anti-knocks (compare the action of carbon). The action of the above inhibitor in the presence of powdered glass or pumice is noteworthy. It has been shown that an increase in the surface thus produced tends to reduce the inhibitory action of the lead tetraethyl, probably owing to an increase in the rate of oxidation. It must be emphasised that the rises of ignition temperatures brought about by this reagent

are entirely different from the foregoing. Lead tetraethyl is a negative catalyst, or anti-oxygen, and delays or inhibits even the initial stage of oxidation, so that very little change occurs in the hydrocarbon at temperatures somewhat higher than the normal ignition point. On the other hand, lead and copper, powdered glass and pumice are promoters of oxidation by surface action and bring about the rise of temperature by a removal of a fraction of the products in one stage of the oxidation which give rise to the explosion.

The spontaneous ignition temperatures are not related to the detonation characteristics of a fuel; thus, the unsaturated hydrocarbons with less knocking tendencies have lower explosion temperatures than the corresponding paraffins. Brown and Watkins (*J. Ind. Eng. Chem.*, 1927, **19**, 368) found that the ratio of the maximum rate of rise of pressure to the ignition temperature (absolute) gives a number which rises directly as the knocking quality of the fuel or inversely as Ricardo's "highest useful compression ratio" (*H.U.C.R.*). The estimated *H.U.C.R.*'s of paraffins and aromatics agree fairly well with those practically determined, but no figures are given for unsaturated hydrocarbons. Since these have correspondingly lower ignition temperatures, it should follow that their maximum rate of rise of pressure is less than that of the corresponding paraffin, and the testing of this point would help to elucidate the problem. In order that fairly accurate results may be obtained for the above ratio, it is essential that the data for auto-ignition be fairly trustworthy. Oftentimes discrepancies are found in the published results, *e.g.*, octane having a higher ignition temperature than heptane, and heptane than hexane. A similar result is shown for decane and octane above, but this is readily explained by the greater oxidisability of decane which is consumed at low temperatures on the surface of the glass, or, in terms of chain mechanism, the deactivation exceeds the rate of chain formation at the lower temperatures, so that it is difficult to make it explode by slow heating. A strict comparison with octane can only be made with equimolecular concentrations of hydrocarbons, equal area and nature of surface, and equal rate of heating. Under such conditions, octane has been shown to ignite before decane, although the rate of heating required for the latter to explode is so rapid that the ignition temperature of octane is somewhat raised above its minimum. The anomalous results obtained by the crucible methods can be explained in a similar manner: the droplets may not have yielded equimolecular concentrations, the rates of heating at the two temperatures are not the same, and at the temperature at which one might expect ignition, the hydrocarbon has been completely removed by flameless or surface combustion, especially when

platinum has been used and the drops have been small. Hence, one unhesitatingly concludes that the method of determining the relative ignitabilities by the measurement of the duration of the pre-flame period or "lag" at a temperature higher than the ignition temperature is to be preferred to the "crucible" experiments. Some of the paraffins have been compared by Mason and Wheeler (J., 1924, 125, 1873) by this method.

The view is prevalent that fuel droplets ignite more easily than the vapour, and this is attributed to the accumulation of peroxides in the liquid drops (Callendar, *Engineering*, 1927, 147). Since extremely low ignition temperatures can be obtained when the concentration of the hydrocarbon and oxygen is high, it is reasonable to suppose that the ignition of the droplets in the above experiments has been favoured by the richness of the vapour-oxygen atmosphere surrounding each liquid particle, thereby bringing about the conditions for the minimum ignition temperature. No significance can be attached to the fact that, when a fuel is sprayed or vaporised through a heated tube, the spray gives rise to a profusion of peroxides whilst the vaporised mixture shows little effect. If peroxides are produced in one stage of the oxidation, this will probably be at the surface of the droplets where they would be absorbed by the comparatively cool liquid and thus preserved. On the other hand, when vapour only is present, the peroxides would eventually come in contact with the heated walls of the tube, with resultant decomposition.

#### *Summary.*

A simple preliminary apparatus has been used to find the conditions and temperature of ignition of mixtures of some hydrocarbons and oxygen, and a mechanism of the reactions has been considered.

Spontaneous ignition temperatures, as determined by the usual methods, are raised by materials, such as lead tetraethyl, which inhibit oxidation or reduce autoxidation, in that they diminish the number of fresh chains formed in unit time, whereas promoters of oxidation by surface action raise the temperature of ignition by removing one of the intermediate products, presumably peroxides, or alternatively, according to the chain mechanism theory, they increase the rate of deactivation.

The disturbing factors in the determination of relative ignition temperatures are so numerous that the measurement of the "lag" in the case of equimolecular concentrations at some point above the ignition temperature is to be preferred as a measure of the ignitabilities of hydrocarbons.

The explosion of hydrocarbons takes place in two stages : (a) the

explosion of the products of autoxidation (peroxides or chain reactions, in which approximately equal number of molecules of oxygen and hydrocarbon participate), and (b) the combustion of the products of stage (a) in excess of oxygen to oxides of carbon and water.

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## XII.—*The Hydrides of Boron.*

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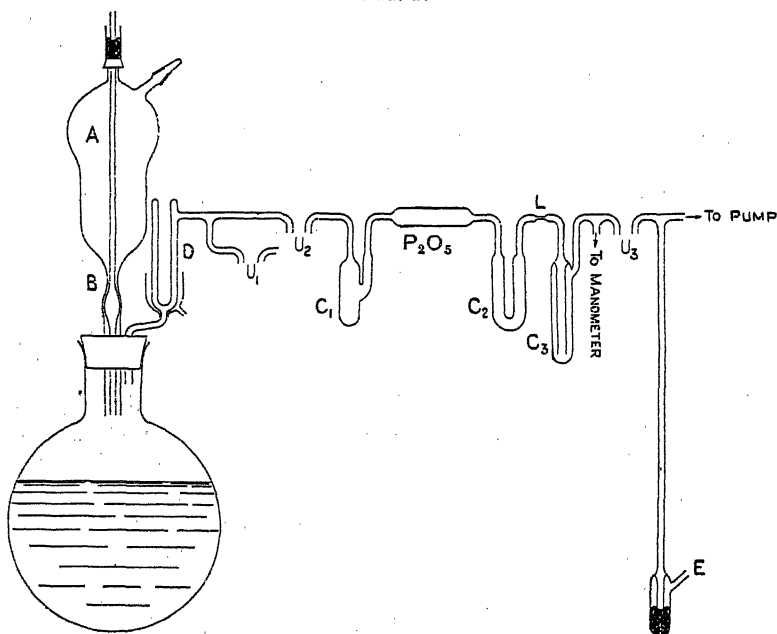
THE investigations of Stock and his collaborators (*Ber.*, 1912 *et seq.*) have definitely shown the existence of a series of boron hydrides of a composition which is unexpected in view of the position of boron in the periodic classification and of the existence of trivalent alkyl compounds. The conclusions of Jones and Taylor (*J.*, 1879, **35**, 41; 1881, **39**, 213), Sabatier (*Compt. rend.*, 1891, **112**, 866), and Ramsay and Hatfield (*P.*, 1901, **17**, 152) as to the existence of  $\text{BH}_3$  are without sufficient experimental foundation, yet a doubt remains that the existence of the simpler hydrides might be established if the field of investigation were widened. All previous investigators have used magnesium boride, except Hoffmann (*Chem.-Ztg.*, 1911, **35**, 265), who showed that commercial iron and manganese borides, on reaction with acids, give boron hydrides, which he did not identify. In the case of carbon, different metallic carbides yield different types of hydrocarbons, and it was suspected that other metallic borides might not yield the same hydrides. The suspicion, however, has not been substantiated.

Wöhler and Deville (*Ann. Chim. Phys.*, 1858, **52**, 63), using high temperatures, prepared borides of aluminium which are practically unreactive with acids, but, by using a method similar to that of Stock and Massenez (*Ber.*, 1912, **45**, 3543) for the preparation of magnesium boride, we have prepared an aluminium boride which reacted with acids to give hydrogen containing boron hydride. The same method, with special precautions, led to the preparation of a cerium boride which reacted similarly. In both cases the yield of boron hydride is small, this being particularly so with the aluminium compound. The identity of our boron hydrides with those formed from magnesium boride has been definitely established in the case of gaseous  $\text{B}_4\text{H}_{10}$ , and although the results in the case of the liquid hydrides are not absolutely decisive, the indications are that they are also the same, namely,  $\text{B}_5\text{H}_9$  and  $\text{B}_6\text{H}_{10}$ .

## EXPERIMENTAL.

*Preparation of the Aluminium Boride.*—Fine aluminium powder (3 parts) and finely powdered boron oxide (1 part) were intimately mixed and fused in small quantities (8–10 g.) in an iron crucible over a large Meker burner. After 3–5 minutes' heating, a bright glow spread through the mass, and at this point the crucible was removed and quickly cooled by plunging its lower portion into water. The product was a greyish, very friable mass.

FIG. 1.



*Preparation of the Cerium Boride.*—Cerium metal powder ( $2\frac{1}{4}$  parts) and powdered boron oxide (1 part) were mixed, and very small quantities fused in a fairly rapid stream of hydrogen. (If large portions were used or if the stream of hydrogen was not rapid, reaction was so vigorous as to melt the bottom of the crucible.) The product, a hard black mass, was powdered in a percussion mortar.

*Generating Apparatus.*—For the decomposition of the boride, phosphoric acid ( $d\ 1.4$ ) at  $75^\circ$  was used. It appears to give better yields than hydrochloric acid, and although some phosphine is formed, this is more readily removed in fractionation than the hydrogen sulphide which results from the use of sulphuric acid.

The acid was placed in a 6-litre flask, and the aluminium or cerium boride in A (Fig. 1), which was closed at the top by a mercury seal through which passed a glass rod with a tapered grinding fitting into a constriction at B. By depressing this rod slightly, and either slowly revolving it or tapping A, the powder could be introduced into the acid at a suitable rate. D was a double-surface water-cooled condenser, and  $C_1$  a condenser immersed in liquid ammonia. The liquid ammonia and finally phosphoric oxide remove water.  $C_2$  was the main condenser immersed in liquid air, and containing cotton wool to prevent any boron hydride passing through as a fume or mist.  $C_3$  was another liquid-air condenser, without cotton wool, and connected to a closed U-tube manometer. The issuing hydrogen bubbled out through mercury at E. The whole was connected to the mercury pump. Owing to the hardening action of the boron hydride on tap lubricant, taps were discarded in favour of either U-tube arrangements with greaseless gas valves (see Stock, *Ber.*, 1914, 47, 3109), or simply U-tubes 80 cm. in length with mercury traps at the top, connected to a mercury reservoir. The positions of these tap substitutes are at  $U_1$ ,  $U_2$ , and  $U_3$ . In case a larger quantity of gas than could be obtained from one charge of A was required,  $U_2$  would be shut when the powder was exhausted, and the air pumped out through  $U_1$  when fresh powder was introduced.

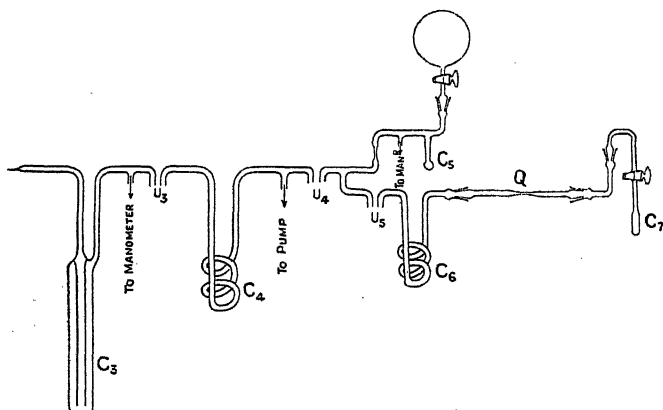
The boron hydride condensed in  $C_2$ , except some of the higher-boiling product, which condensed in the liquid ammonia. In no case did the issuing hydrogen burn with a green flame. When all the gas had been generated,  $U_2$  was shut, the hydrogen pumped out, and the condensate transferred to the condenser without cotton wool, any boron hydride in the liquid ammonia being transferred also. A constriction at L was then sealed off,  $U_3$  shut, and the glass tubing to the right of it cut and joined to the fractionating and analysing apparatus shown in Fig. 2, all the air being then pumped out.

*Fractionation and Analysis.*—By blowing liquid air through pentane in a Dewar vessel, a range of temperature up to  $-120^\circ$  could be attained, the temperature being measured by a standardised pentane thermometer. Fractionation was carried out at selected temperatures, the pressure shown by the manometer being read;  $U_3$  was opened for a short interval, thus allowing passage to  $C_4$  in liquid air, then closed again, and the manometer re-read, the process being repeated if necessary. The fraction thus removed and condensed in  $C_4$  was then analysed without interfering with the residue of the yield,  $U_3$  being kept shut and  $C_3$  replaced in liquid air. The liquid air was removed from  $C_4$ , and the fraction allowed to vaporise



into the density bulb. Since we were dealing with small quantities, we condensed all the fraction in  $C_5$  by liquid air, shut  $U_4$  and  $U_5$ , and then removed the liquid air. The pressure was read on the manometer, the tap to the density bulb shut, and the small amount of gas in the connecting tubes pumped out and collected. When the bulb was replaced after weighing and the air pumped out, the tap to the bulb was opened and the gas condensed by liquid air in  $C_7$ , where it was reweighed. By removing the liquid air from under  $C_7$  the gas was allowed to stream through a quartz tube  $Q$ , which was heated to redness. Unless the passage of the gas is very slow, decomposition is not complete.  $C_6$  was kept in liquid air to collect undecomposed gas. The hydrogen was pumped out and its volume measured. Any undecomposed gas was then transferred by liquid

FIG. 2.



air back to  $C_7$ , and the process repeated. Any solid boron hydride formed in the cooler part of the tube was decomposed by strong heating. Entire decomposition was assured. The deposited boron was estimated both by direct weighing and by titration as boric acid after oxidation by nitric acid. A further study of the composition was afforded by reaction with strong alkali solution, and then decomposition of any hypoborate formed by addition of excess of sulphuric acid; for this purpose, in the case of  $B_4H_{10}$  an amount was pumped out and its volume measured, and in the case of the higher-boiling fractions an amount in  $C_7$  was weighed. The reaction is  $B_xH_y + 3xH_2O = xH_3BO_3 + \frac{1}{2}(3x + y)H_2$ .

The results leave no doubt as to the formation of  $B_4H_{10}$  from both the aluminium and the cerium compound. The results given by the liquid fractions are not quite so definite, but indicate  $B_5H_9$  and  $B_6H_{10}$ .

Silicon hydrides, phosphine, and carbon dioxide are formed from the aluminium compound and phosphoric acid. Phosphine and carbon dioxide, but no silicon hydrides, are formed from the cerium compound.

*Results from Cerium Boride.*—280 G. of the boride and 4 litres of phosphoric acid were used. The earlier fractions proved on analysis to be mixtures of phosphine and carbon dioxide, with no trace of boron hydride. The hydride was first detected in a fraction at  $-90^{\circ}/<1$  mm. The fraction taken at  $-80^{\circ}$  with a constant vapour pressure (about 1 mm.) gave the following results:

Volume = 12—15 c.c.

- (a) Molecular weight, 52.5 (Calc. for  $B_4H_{10}$ , 54).
- (b) Decomposition by water: 1 vol.  $\rightarrow$  10.7 vols. (Calc., 11 vols.).
- (c) Decomposition by heat: 4.5 c.c. (at 765 mm. and  $22^{\circ}$ ) gave 22.3 c.c. of hydrogen (Calc., 22.5 c.c.) and a deposit of boron—(1) by weight = 8.5 mg., (2) by titration = 8.2 mg. (Calc., 8.3 mg.).

The next fractionation, carried out at the temperature of liquid ammonia ( $-33^{\circ}$ ), gave 35 mg. of a liquid; the residue (about 10 mg.) was not analysed.

(a) Decomposition by water: 6.4 mg. gave 26.8 c.c.  $H_2$  at N.T.P. (Calc.: For  $B_6H_{10}$ , 26.1 c.c.; for  $B_5H_9$ , 26.6 c.c.; for  $B_4H_{10}$ , 28.9 c.c.).

(b) Decomposition by heat: 28.7 mg. gave 24.6 mg. of boron and 45.5 c.c. or 4.1 mg. of hydrogen (Calc.: For  $B_4H_{10}$ , 23.4 mg. B, 5.3 mg.  $H_2$ ; for  $B_5H_9$ , 24.7 mg. B, 4.0 mg.  $H_2$ ; for  $B_6H_{10}$ , 24.9 mg. B, 3.8 mg.  $H_2$ ).

This fraction probably contained some  $B_4H_{10}$ , and the analyses are probably those of a mixture of  $B_4H_{10}$ ,  $B_5H_9$ , and  $B_6H_{10}$ —the  $B_4H_{10}$  in small amount.

*Results from Aluminium Boride.*—800 G. of the boride were used. Early fractions contained no boron hydride. The fraction (about 15 c.c.) at b.p.  $-80^{\circ}/1$  mm. gave:

- (a) Molecular weight, 55.05.
- (b) Decomposition by water: 1 vol.  $\rightarrow$  10.8 vols. of  $H_2$ .
- (c) „ „ heat: 1 vol.  $\rightarrow$  5.05 vols. of  $H_2$ .

The next fraction was taken at  $-60^{\circ}$ . It was too small to be analysed, but probably contained the last of the  $B_4H_{10}$ .

Two fractions were taken at  $-33^{\circ}$ ; the first (10 mg.) was lost, but the second (20 mg.) gave a result agreeing very closely with

$B_6H_{10}$  : 10.45 mg. gave 15.4 c.c.  $H_2$  at *N.T.P.* and 9.0 mg. B (calc. for  $B_6H_{10}$  : 15.2 c.c.  $H_2$ , 9.1 mg. B).

In conclusion, the authors wish to express their thanks to the Trustees of the Commonwealth Science and Industry Endowment Fund for a grant which helped to defray the expenses of the research.

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### XIII.—*Acid and Salt Effects in Catalysed Reactions.* *Part XXIII. The Catalytic Activity of Acid Salts with Reference to the Catalytic Effects produced by Potassium Hydrogen Oxalate in the Acetone-Iodine Reaction.*

By HARRY MEDFORTH DAWSON and JESSE EYRE SMITH.

IN two previous papers (Dawson, Hoskins, and Smith, J., 1929, 1884; Dawson and Smith, *ibid.*, p. 2530) an account has been given of the catalytic effects associated with oxalic acid in the first and second stages of ionisation. The experimental work relates to the effects produced by mixtures of acid and salt represented respectively by  $cH_2C_2O_4 + xKHC_2O_4$  and  $cKHC_2O_4 + xK_2C_2O_4$ , where  $c$  is constant and  $x$  is variable, and further, to the influence of inert salts on the primary and secondary ionisation of oxalic acid. The relations disclosed by these observations permit us to proceed to the detailed consideration of the catalytic properties of solutions of the binoxalate.

The interesting problem presented by the catalytic activity of the acid salts of polybasic acids does not appear to have been subjected to systematic investigation, and the results of the present enquiry indicate that their behaviour cannot be explained in terms of any form of the simple hydrogen-ion theory.

The hydrogen-ion concentration of solutions of an acid salt of the type MHA is given by

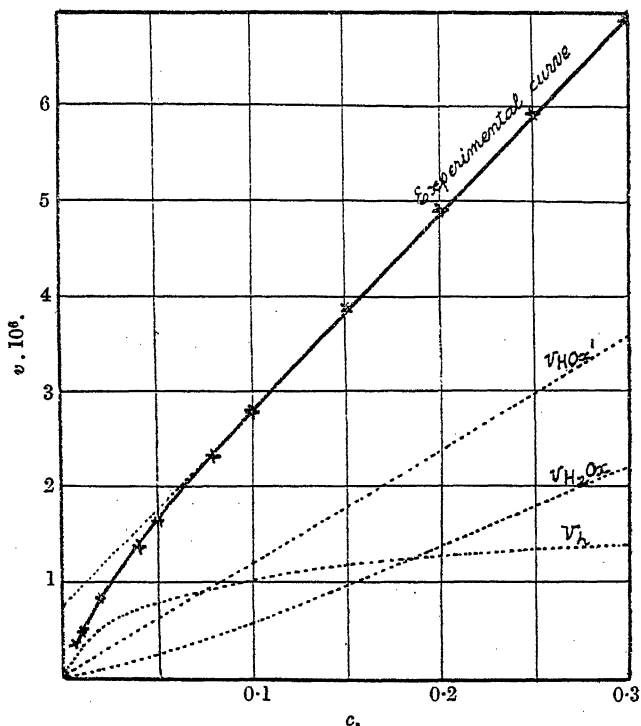
$$[H^+] = \sqrt{K_1 K_2 [HA'] / (K_1 + [HA'])}$$

where  $K_1$  and  $K_2$  are the mass-law constants for the first and second stages of dissociation of the acid  $H_2A$ . This reduces to  $[H^+] = \sqrt{K_1 K_2}$  if the concentration ( $c$ ) of the acid salt is large compared with  $K_1$ , and to  $[H^+] = \sqrt{K_2(c - [H^*])}$  if  $c$  is small in comparison with  $K_1$ . If  $K_2$  is small the latter expression becomes  $[H^+] = \sqrt{K_2 c}$ . In so far as the hydrogen ion is responsible for the catalytic effects in the

solutions of an acid salt, it may therefore be anticipated that the connexion between the reaction velocity and the concentration of the acid salt will depend on the relative magnitudes of  $c$  and  $K_1$ .

The restricted solubility of the binoxalates imposes a rather low upper limit to the range of concentration of the solutions which may be used for the study of the catalytic effects. In pure aqueous solution, the range extends from about  $c = 0.01$  to  $c = 0.3$  mol. per

FIG. 1.



Plot of reaction velocity against concentration. The full curve represents the experimental data and shows the deviations from linearity at low concentrations. The dotted curves show the variation of the partial velocities  $v_h$ ,  $v_{H_2Ox}$ , and  $v_{HOx}$ .

litre, and since the mean value of  $K_1$  for this series of solutions may be taken as 0.08, it follows that  $c$  is less than  $K_1$  for the less concentrated, and greater than  $K_1$  for the more concentrated solutions of the series. This circumstance has a direct bearing on the relations which are shown by the measured reaction velocities.

The observations were made at  $25^\circ$  with an acetone concentration of 20.0 c.c. per litre, and the usual procedure was followed in determining the initial velocity. By plotting this against the concen-

tration, it is found (see Fig. 1) that the velocity varies almost linearly with the concentration when  $c > 0.1$ , but that at lower concentrations  $dv/dc$  increases as  $c$  diminishes.

In accordance with previous results, the specific reaction velocity may be represented by the equation

$$v = k_h[H'] + k_{H_2Ox}[H_2Ox] + k_{HOx'}[HOx'] + k_{Ox''}[Ox''] \quad (1)$$

in which the concentrations of the various catalytic entities are given by

$$[H'] = \sqrt{K_1 K_2 [HOx'] / (K_1 + [HOx'])}, [H_2Ox] = [H'] [HOx'] / K_1, \\ [HOx'] = c - [H'] - 2[H_2Ox], \text{ and } [Ox''] = [H'] + [H_2Ox].$$

The magnitude of the ionisation constants and of the catalytic coefficients varies with the nature and concentration of the ionic environment and such variations must be taken into account as far as possible in the application of equation (1).

Since the binoxalate ion is neither catalytically nor chemically inert, it is not possible to determine the inert-salt effects peculiar to an atmosphere of potassium and binoxalate ions by the methods which are permissible in the case of solutions of salts which are both chemically and catalytically inert. In these circumstances it has been assumed that the values of  $K_1$  and  $K_2$  for the binoxalate solutions are the same as for the corresponding solutions of potassium chloride. For the latter it has been shown (*loc. cit.*) by experiments relating to the first and second stages of ionisation that the values are given by

$$\log K_1 = 2.756 + 0.42\sqrt{x} - 0.275x$$

and

$$\log K_2 = 5.857 + 0.81\sqrt{x} - 0.39x,$$

in which  $x$ , the total salt concentration, corresponds in the present paper with the molar concentration ( $c$ ) of the binoxalate.

With regard to the variations in the catalytic coefficients, it may be recalled that the available evidence would seem to show that the hydrogen ion is considerably more susceptible than other catalytic entities to changes in environment. The effects in question are specific in the sense that they depend on the nature of the ions in the solution, and as already pointed out, they cannot be determined for a solution of potassium binoxalate. Since, however, the maximum salt concentration in our experiments is only 0.3 mol. per litre, it is permissible as a first approximation to assume that  $k_h$  is not affected by the presence of the binoxalate. In support of this procedure, it may be noted that the catalytic effect due to the hydrogen ion in the more concentrated solutions is only a small fraction of the total effect. The reaction velocities recorded in

Table I are therefore based on the following values for the various catalytic coefficients, *viz.*,  $k_h = 465 \times 10^{-6}$ ,  $k_{H_2Ox} = 210 \times 10^{-6}$ ,  $k_{HOx} = 13.0 \times 10^{-6}$ , and  $k_{Ox''} = 1 \times 10^{-6}$ . The first column gives the concentration of the binoxalate; the second, third, fourth, and fifth give the partial velocities due to the hydrogen ion, the undissociated oxalic acid, the binoxalate ion, and the oxalate ion respectively; the sixth shows the calculated, and the seventh the observed velocity.

TABLE I.

Catalytic activity of aqueous solutions of potassium hydrogen oxalate.

c.	$v_h \cdot 10^6$	$v_{H_2Ox} \cdot 10^6$	$v_{HOx} \cdot 10^6$	$v_{Ox''} \cdot 10^6$	$v \cdot 10^6$ (calc.).	$v \cdot 10^6$ (obs.).
0.005	0.270	0.009	0.056	—	0.335	0.315
0.01	0.382	0.025	0.111	0.001	0.52	0.49
0.02	0.535	0.069	0.235	0.001	0.84	0.82
0.04	0.72	0.175	0.480	0.002	1.37	1.37
0.05	0.79	0.24	0.60	0.003	1.63	1.62
0.08	0.94	0.44	0.96	0.004	2.34	2.32
0.10	1.02	0.58	1.20	0.005	2.80	2.79
0.15	1.16	0.97	1.79	0.007	3.93	3.88
0.20	1.27	1.37	2.39	0.009	5.04	4.91
0.25	1.36	1.79	2.99	0.011	6.15	5.90
0.30	1.43	2.22	3.59	0.014	7.25	6.90

The autocatalytic effect of the hydriodic acid produced in the reaction sets a lower limit to the concentration of the binoxalate solutions for which the reaction velocity can be measured with accuracy. Within the available range of concentrations it is clear from the table that equation (1) affords a satisfactory account of the measured velocities. The systematic divergence at the higher concentrations suggests that the increase in  $K_1$  and  $K_2$  may not be so great for the binoxalate as for the corresponding chloride.

By plotting the partial velocities against the concentration of the acid salt, it is found that  $v_{HOx}$  is a linear function of  $c$ , and  $v_{H_2Ox}$  very nearly so when  $c$  is greater than 0.1, whilst  $v_h$  tends towards a maximum value. These relations are consistent with the fact that the experimental  $v$ - $c$  curve is approximately linear for  $c > 0.1$ . The slope of this linear portion of the curve corresponds with  $dv/dc = 20 \times 10^{-6}$ , and when extrapolated to  $c = 0$ , the line in question is found to cut the zero ordinate at about  $v = 0.8 \times 10^{-6}$ , which, it may be noted, is nearly three times as great as the velocity at the smallest concentration. In connexion with this very considerable initial velocity which seems to be indicated by the linear portion of the experimental  $v$ - $c$  curve, it may be recalled that the hydrogen-ion concentration approximates to the value  $[H'] = \sqrt{K_1 K_2}$  when  $c$  becomes large in comparison with  $K_1$ . If this value of  $[H']$  is

combined with the stoicheiometric equation  $c = [\text{H}_2\text{Ox}] + [\text{HOx}'] + [\text{Ox}']$  and the mass-action expressions

$$K_1 = [\text{H}'][\text{HOx}']/[\text{H}_2\text{Ox}] \text{ and } K_2 = [\text{H}'][\text{Ox}']/[\text{HOx}']$$

we obtain

$$[\text{H}_2\text{Ox}] = c[\text{H}']^2/([\text{H}']^2 + K_1[\text{H}'] + K_1K_2) = c\sqrt{K_2}/(\sqrt{K_1} + 2\sqrt{K_2})$$

$$[\text{HOx}'] = cK_1[\text{H}']/([\text{H}']^2 + K_1[\text{H}'] + K_1K_2) = c\sqrt{K_1}/(\sqrt{K_1} + 2\sqrt{K_2})$$

and

$$[\text{Ox}'] = cK_1K_2/([\text{H}']^2 + K_1[\text{H}'] + K_1K_2) = c\sqrt{K_2}/(\sqrt{K_1} + 2\sqrt{K_2})$$

Putting  $\sqrt{K_2}/(\sqrt{K_1} + 2\sqrt{K_2}) = \gamma$  and  $\sqrt{K_1}/(\sqrt{K_1} + 2\sqrt{K_2}) = \delta$ , and substituting the values of  $[\text{H}']$ ,  $[\text{H}_2\text{Ox}]$ ,  $[\text{HOx}']$ , and  $[\text{Ox}']$  in equation (1), the latter becomes

$$v = k_h\sqrt{K_1K_2} + \{(k_{\text{H}_2\text{Ox}} + k_{\text{Ox}'})\gamma + k_{\text{HOx}'}\delta\}c. \quad (2)$$

according to which, apart from variations in  $K_1$  and  $K_2$ , the  $v$ - $c$  curve should be a straight line the slope of which is given by the value of  $(k_{\text{H}_2\text{Ox}} + k_{\text{Ox}'})\gamma + k_{\text{HOx}'}\delta$ . Since  $\gamma$  and  $\delta$  are not greatly affected by the variations in  $K_1$  and  $K_2$ , the slope may be determined with some precision. If, for instance, we utilise the values of  $K_1$  and  $K_2$  which correspond with  $c = 0.2$ , namely,  $K_1 = 7.8 \times 10^{-2}$  and  $K_2 = 14 \times 10^{-5}$ , then  $\gamma = 0.039$  and  $\delta = 0.93$ , and for  $(k_{\text{H}_2\text{Ox}} + k_{\text{Ox}'})\gamma + k_{\text{HOx}'}\delta$  we obtain  $20.3 \times 10^{-6}$ , which agrees closely with the slope of the linear portion of the experimental curve.

The term  $k_h\sqrt{K_1K_2}$  in the above velocity equation obviously corresponds with the initial velocity which is indicated when the approximately linear  $v$ - $c$  curve is extrapolated to  $c = 0$ . This curve is actually slightly concave to the  $c$  axis, which means that the slope of the tangent decreases and therefore that the intercept on the zero concentration ordinate increases as the value of  $c$  increases. This may be due in part to the circumstance that the hydrogen-ion concentration has not reached the value represented by  $\sqrt{K_1K_2}$  within the range of the concentrations actually used, but it is also quite probably attributable in part to the increase in  $K_1$  and  $K_2$  which occurs when the concentration increases. In any case, the velocity measurements are not accurate enough to permit of the determination of the variation of the intercept with the concentration of the binoxalate, and it must suffice to record the fact that linear extrapolation of the velocities for the higher concentrations leads to a velocity for  $c = 0$  which corresponds fairly closely with the magnitude  $k_h\sqrt{K_1K_2}$ .

To provide further support for the conclusions suggested by the data recorded in Table I, a parallel series of measurements has been made with solutions in which the ionic strength was kept constant at  $\mu = 0.3$  by the addition of potassium chloride. This series is represented by  $c\text{KHC}_2\text{O}_4 + (0.3 - c)\text{KCl}$ . In the application of equation (1) to these solutions, the constant values taken for  $K_1$  and  $K_2$  are those corresponding with  $0.3M$ -potassium chloride, and the value of  $k_h$  is assumed to be determined by the potassium chloride content of the solutions. The arrangement of Table II, in which the results are recorded, is exactly similar to Table I.

TABLE II.

Catalytic activity of potassium hydrogen oxalate in solutions of constant ionic strength ( $\mu = 0.3$ ).

$c$ .	$v_h \cdot 10^6$ .	$v_{\text{H}_2\text{Ox}} \cdot 10^6$ .	$v_{\text{HOx}'} \cdot 10^6$ .	$v_{\text{Ox}''} \cdot 10^6$ .	$v \cdot 10^6$ (calc.).	$v \cdot 10^6$ (obs.).
0.02	0.74	0.07	0.23	0.002	1.04	1.09
0.04	0.965	0.185	0.47	0.003	1.62	1.67
0.08	1.19	0.46	0.95	0.005	2.60	2.59
0.10	1.24	0.60	1.19	0.005	3.04	3.05
0.15	1.34	0.99	1.79	0.008	4.13	4.08
0.20	1.39	1.39	2.39	0.010	5.18	4.99
0.25	1.42	1.80	2.98	0.012	6.21	5.94
0.30	1.43	2.22	3.59	0.014	7.25	6.90

The  $v$ - $c$  curve corresponding to the second series of observations is of the same general character as the curve for the chloride-free solutions and need not be discussed in detail. There is, of course, no suggestion that constancy of ionic strength affords conditions of ionic environment which entitle the results in Table II to be regarded as strictly comparable. The combined results for the two series afford, however, considerable justification for the belief that inert-salt effects, in so far as they have not been allowed for, are of very minor significance, and that equation (1) provides a satisfactory basis for the interpretation of the experimental data.

Both sets of observations show that the connexion between the reaction velocity and the concentration of the acid salt varies with the latter. The connexion is approximately linear for the more concentrated solutions of the series. The hydrogen-ion concentration of these solutions varies within very narrow limits and the observed catalytic effects are mainly due to the binoxalate ion and the undissociated oxalic acid, the concentrations of which vary linearly with the total concentration of the acid salt. In the more dilute solutions, on the other hand, the dominant catalyst is the hydrogen ion, and as the concentration falls there is a gradual



approach to a condition in which the reaction velocity is essentially determined by the hydrogen-ion concentration.

The results show conclusively that the catalytic activity of acid salts is in large measure due to the catalytic action of the acid ion ( $\text{HA}'$ ) and of the undissociated acid ( $\text{H}_2\text{A}$ ).

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#### XIV.—*The Routine Preparation of Conductivity Water. Part II.*

By JOHN M. STUART and FRANK WORMWELL.

NEARLY five years' experience in the preparation of large quantities of conductivity water has shown the desirability of certain modifications in the still previously described (J., 1927, 2156). After about two years' work, minute cracks developed where the narrowed portion of tube ( $d$  in Fig. 1 of that paper) joined the main condensing column, and, later, this column became constricted where it is held by a retort clamp just above the lower jacket.

A modified design (Figs. 1 and 2 of present paper) has now been adopted. The tin condensing column C is placed vertically above the tinned-copper steam-trap to which it is connected by a copper tube A, tinned inside and flanged at each end. The top copper flange D is tin-soldered to the lower flanged end of this condensing column, the weight of which is carried on the steam trap B, Fig. 2. The joints of this, shown at S in Fig. 2, are silver-soldered. The trap itself is carried on vertical steel rods arranged as in the earlier still; the only clamp required is one to steady the top of the condensing column.

The condensed water collects in a circular trough T, formed between a short length of tin tube and the inner wall of the condensing column; from this it flows along a short horizontal water-jacketed tin tube H, where it meets a stream of purified air from the tube K; thence it passes through a glass condenser, the outlet of which is formed into a horizontal T-piece, the lower tube of which is connected to the conductivity measuring cell. The arrangement permits a thermometer to be placed vertically in the water in the conductivity cell itself; this is desirable, for the temperature varies between about  $17^\circ$  and  $25^\circ$ , with appreciable effect on the conductivity.

In the main condensing column there is a piece of pure sheet tin bent so as to break up the main column of steam rising straight up from the trap, and ensure its thorough mixture with the

stream of purified air from tube H. This tin was introduced when the still had only been run for a few days, the conductivity of the water being then about  $0.15 \times 10^{-6}$  mho. Shortly afterwards a steady decrease in conductivity occurred, which may, however, have been the usual improvement due to the gradual washing out of impurities from a newly erected still.

All soldered joints in the condensing column are made with pure tin. Before finally fixing the condensing column in position it

FIG. 1.

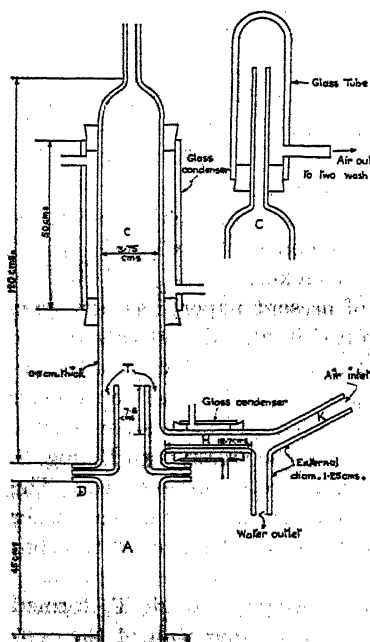
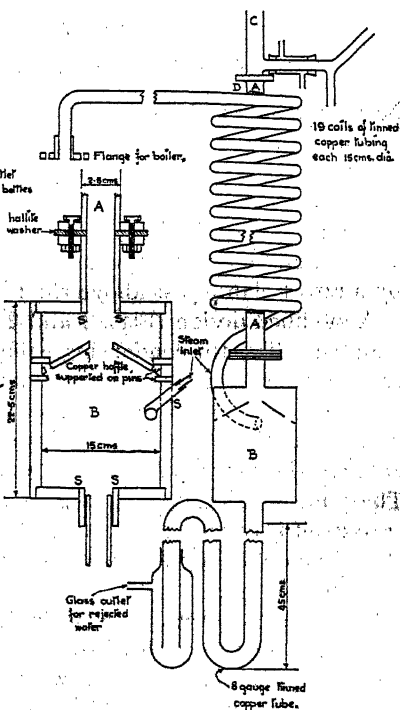


FIG. 2.



should be washed out with carbon tetrachloride and thoroughly steamed. The Weiland air-purification train originally used and illustrated in Fig. 1 of the earlier paper was found to be inconvenient for continuous use owing to sticking taps. The form of train now used consists of four columns, 3 cm. in diameter and 45 cm. high, containing glass beads and joined together by short lengths of rubber tubing so that they can be separated for refilling, thus rendering taps unnecessary. The presence of rubber in the air train does not appear to affect the conductivity of the water.

A typical day's run with the still is recorded below. The temper-

ature is that of the water in the cell, and  $\kappa$  is its conductivity in gemmhos, corrected to 18°.

Time.	Temp.	$\kappa$ .	Time.	Temp.	$\kappa$ .	Time.	Temp.	$\kappa$ .
11.40 a.m.	20.6°	0.090	1.10 p.m.	22.1°	0.057	3.05 p.m.	20.5°	0.058
11.47	20.9	0.067	1.28	21.6	0.055	3.27	20.5	0.060
12.05 p.m.	21.4	0.064	1.43	21.5	0.055	3.50	20.1	0.062
12.22	21.9	0.057	2.03	20.4	0.056	4.10	21.4	0.062
12.40	21.1	0.057	2.22	21.3	0.058	4.30	21.6	0.063
12.57	21.8	0.057	2.43	21.3	0.058			

Total volume of conductivity water collected from 11.40 a.m. to 4.30 p.m. = 4555 c.c.

Total volume of water rejected at trap = 2300 c.c.

The conductivities so far obtained are much the same as those of the older still when both are run simultaneously, but the latter occasionally gives very low values, *e.g.*, 0.047 at 18°. Probably, after a few months' use, the new still will give similar results—the best hitherto is  $\kappa = 0.053$  at 18°.

The advantages claimed for the modified design are low cost, great strength and compactness, ease of erection and working, and durability. The actual still occupies a bench length of 110 cm. or, including the air-purification train, 2 m. It quickly gives good-quality water which, at its best is rather better than that from such stills as that of Bencovitch and Hotchkiss (*J. Physical Chem.*, 1925, 29, 705).

The authors wish to thank Mr. R. May for advice on the construction of the still, and Professor G. T. Morgan for permission to publish the results.

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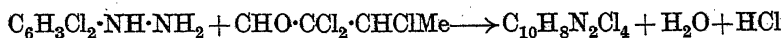
## XV.—*The Interaction of Butyl Chloral Hydrate and 2:4-Dihalogen-substituted Phenylhydrazines.*

By FREDERICK DANIEL CHATTAWAY and HARRY IRVING.

WHEN butyl chloral hydrate reacts with phenylhydrazine, the hydrazone initially formed decomposes almost at once with such violence that the course of the reaction cannot easily be followed. When, however, a 2:4-dihalogen-substituted phenylhydrazine is used, the decomposition proceeds more quietly and the final products can be isolated. As in the reactions between the halogen-substituted phenylhydrazines and ordinary chloral (Chattaway and Bennett, 1927, 2850; Chattaway and Daldy, J., 1928, 2756), these final

products differ according to the nature of the solvent in which the reaction takes place.

The first product of the interaction of butyl chloral hydrate and 2 : 4-dichlorophenylhydrazine hydrochloride in aqueous solution is a viscous crimson mass which cannot be obtained in a condition suitable for analysis, since, from the moment of its formation, whether alone or in contact with a solvent, it continually evolves hydrogen chloride, yielding finally a well-crystallised substance of the composition  $C_{10}H_8N_2Cl_4$ . This appears to have been formed from a molecule of butyl chloral and a molecule of 2 : 4-dichlorophenylhydrazine by the elimination of a molecule of water and a molecule of hydrogen chloride :



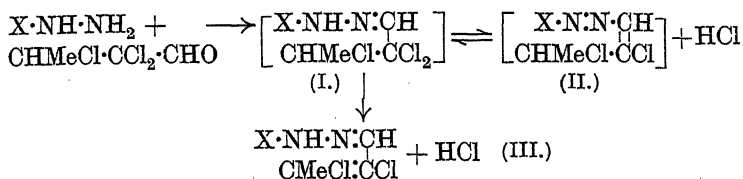
When strongly reduced, it yields 2 : 4-dichloroaniline; the halogen atom eliminated in the reaction must therefore have been one of those in the butyl chloral residue. Its pale yellow colour indicates that, unlike the compound formed in the corresponding reaction of ordinary chloral, it has no azo-linkage in its molecule. It is unsaturated and combines directly with two atoms of bromine to give a colourless *dibromo*-addition compound,  $C_{10}H_8N_2Cl_4Br_2$ . With acetic anhydride it yields a colourless *monoacetyl* derivative, pointing to the presence of a single imino-group in the molecule. This acetyl derivative is still unsaturated and gives on careful chlorination a colourless dichloro-addition compound of the composition  $C_{10}H_7N_2Cl_4(CO \cdot CH_3)Cl_2$ .

These reactions appear to show that it is  $\alpha\beta$ -*dichlorocrotonaldehyde*-2 : 4-*dichlorophenylhydrazone* (III) formed by the elimination of hydrogen chloride from the unstable butyl chloral 2 : 4-dichlorophenylhydrazone (I) which is without doubt formed initially.

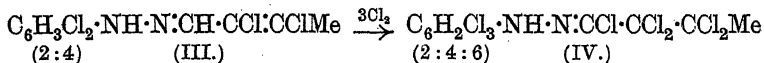
As in the analogous reactions between halogen-substituted phenylhydrazines and chloral (see above), or dichloroacetaldehyde (Chattaway and Farinholt, this vol., p. 94), it seems probable that butyl chloral 2 : 4-dichlorophenylhydrazone also loses hydrogen chloride in a reversible manner to give a crimson azobutylene derivative of the constitution  $C_6H_3Cl_2 \cdot N \cdot N \cdot CH : CCl \cdot CHClMe$ , 2 : 4-dichlorobenzeneazo- $\beta\gamma$ -dichloro- $\Delta^a$ -butylene (II).

In virtue of its azo-structure this compound would be intensely red and, although it is not formed to an extent large enough to permit of its isolation, it nevertheless gives a deep crimson azo-colour to the viscid mass obtained in the early stage of the condensation.

The course of the reaction where  $X = C_6H_3Cl_2(2 : 4)$  may be represented as follows :

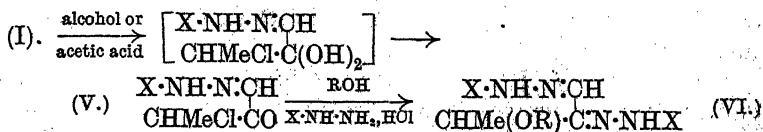


Although  $\alpha\beta$ -dichlorocrotonaldehyde-2:4-dichlorophenylhydrazone (III) combines readily with two atoms of bromine at the ordinary temperature and without further substitution, a similar addition compound with chlorine cannot be obtained, since simultaneous substitution always takes place. The final product of the chlorination is  $\alpha\alpha\beta\beta\omega$ -pentachlorobutaldehyde-2:4:6-trichlorophenylhydrazone (IV), in which two atoms of chlorine have added on to the double bond, a third has entered the nucleus, and a fourth has displaced the methine hydrogen atom:



When butyl chloral hydrate and 2:4-dichlorophenylhydrazine hydrochloride react in alcohol or acetic acid, the reaction pursues a different course and a well-crystallised yellow compound (V) of the composition  $\text{C}_{10}\text{H}_9\text{ON}_2\text{Cl}_3$  is ultimately obtained. This appears to have been derived from butyl chloral 2:4-dichlorophenylhydrazone (I) by replacement of two atoms of chlorine by an atom of oxygen. When strongly reduced, it yields 2:4-dichloroaniline; the halogen atoms lost in the decomposition must therefore have been in the butyl chloral residue. Its yellow colour indicates that there is no azo-group in the molecule, and the presence of an imino-group is established by the formation of a colourless monobenzoyl derivative,  $\text{C}_{10}\text{H}_8\text{ON}_2\text{Cl}_3(\text{CO} \cdot \text{C}_6\text{H}_5)$ .

It must therefore have the structure  $\beta$ -chloro- $\alpha$ -ketobutaldehyde-2:4-dichlorophenylhydrazone (V). When heated with a substituted phenylhydrazine in any alcoholic solution, it yields a sparingly soluble osazone (VI) in which the ketonic oxygen has been replaced by a hydrazine residue, and also the one remaining chlorine atom in the aldehyde residue has been simultaneously replaced by an alkoxy-group:



When the reaction between butyl chloral hydrate and 2:4-dichlorophenylhydrazine hydrochloride is carried out in methyl

alcohol, the latter reaction takes place so readily that the ketonic hydrazone (V) and the sparingly soluble methoxyl-osazone (VI) are formed together, but they may be separated by fractional crystallisation.

#### EXPERIMENTAL.

*The Action of 2:4-Dichlorophenylhydrazine Hydrochloride on Butyl Chloral Hydrate in Water: Formation of  $\alpha\beta$ -Dichlorocrotonaldehyde-2:4-dichlorophenylhydrazone (III).*—To 20 g. (1 mol.) of 2:4-dichlorophenylhydrazine hydrochloride dissolved in 1000 c.c. of water at 75° acidified with 5 c.c. of concentrated hydrochloric acid, was added a solution of 18 g. (1 mol.) of butyl chloral hydrate and 13 g. of sodium acetate in 250 c.c. of water, also at 75°. The liquid immediately became turbid owing to the separation of yellow oily droplets, which turned first pink and then red, finally coalescing to form a viscous crimson mass. When cold, the supernatant liquid was decanted and the red viscous material was extracted with chloroform, in which it was readily soluble. The chloroform solution, after drying over calcium chloride, was kept at the ordinary temperature in an open dish for 4 days until the evolution of hydrogen chloride, which had been continuous from the first, had apparently ceased.

The chloroform had then evaporated, leaving a semi-crystalline mass. The crystals were separated, washed free from viscous material with light petroleum, and recrystallised repeatedly from boiling alcohol (animal charcoal).

*$\alpha\beta$ -Dichlorocrotonaldehyde-2:4-dichlorophenylhydrazone* crystallises from boiling alcohol or acetic acid, in which it is readily soluble, in pale yellow, long, slender, flattened prisms, m. p. 112° (Found: C, 40.5; H, 3.0; N, 9.4; Cl, 47.7.  $C_{10}H_8N_2Cl_4$  requires C, 40.3; H, 2.7; N, 9.4; Cl, 47.65%).

*Reduction of  $\alpha\beta$ -Dichlorocrotonaldehyde-2:4-dichlorophenylhydrazone.*—5 g. of the hydrazone were dissolved in 20 c.c. of glacial acetic acid and boiled with excess of granulated tin and 20 c.c. of concentrated hydrochloric acid. When the pale yellow colour had completely disappeared (1 hour), the hot solution was made alkaline with aqueous caustic soda and steam-distilled. 2:4-Dichloroaniline (1 g.) in the distillate was identified by conversion into its acetyl derivative, which, alone or mixed with an authentic specimen, melted at 145.5°.

*The Action of Bromine upon  $\alpha\beta$ -Dichlorocrotonaldehyde-2:4-dichlorophenylhydrazone.*—When bromine (1 mol.), dissolved in a few c.c. of glacial acetic acid, was added to a cold saturated solution of the hydrazone in glacial acetic acid,  $\alpha\beta$ -dichloro- $\alpha\beta$ -dibromocrotonaldehyde-2:4-dichlorophenylhydrazone separated. It dissolved

readily in hot glacial acetic acid, from which it separated in colourless compact prisms, m. p. 126—127° (decomp.) (Found: Cl, 31.3; Br, 35.3.  $C_{10}H_8N_2Cl_4Br_2$  requires Cl, 31.0; Br, 34.9%).

*Action of Chlorine upon  $\alpha\beta$ -Dichlorocrotonaldehyde-2:4-dichlorophenylhydrazone.*—A rapid stream of chlorine was passed into a suspension of 6.5 g. of the hydrazone in 20 c.c. of glacial acetic acid. The temperature rose somewhat, hydrogen chloride was freely evolved, and the solid dissolved, giving an almost colourless solution. When no further change appeared to be taking place ( $\frac{1}{2}$  hour), the solution was set aside for 24 hours, during which  $\alpha\alpha\beta\beta\omega$ -pentachlorobutaldehyde-2:4:6-trichlorophenylhydrazone (IV) (7.6 g.) slowly separated. It crystallised from boiling acetic acid or alcohol, in which it was readily soluble, in very slender, colourless prisms, m. p. 84—85° (Found: Cl, 64.7.  $C_{10}H_6N_2Cl_8$  requires Cl, 64.8%).

*Reduction of  $\alpha\alpha\beta\beta\omega$ -Pentachlorobutaldehyde-2:4:6-trichlorophenylhydrazone.*—2 G. of the octachloro-compound were reduced by boiling in acetic acid solution with tin and hydrochloric acid. 2:4:6-Trichloroaniline, separated from the solution, made alkaline, by steam distillation, was identified by conversion into its acetyl derivative, m. p. 208—209°.

*Acetylation of  $\alpha\alpha\beta\beta\omega$ -Pentachlorobutaldehyde-2:4:6-trichlorophenylhydrazone.*—A solution of the hydrazone in acetic anhydride containing a drop of concentrated sulphuric acid was boiled for several minutes. On cooling,  $\alpha\alpha\beta\beta\omega$ -pentachlorobutaldehyde-N-acetyl-2:4:6-trichlorophenylhydrazone separated. It crystallised from boiling acetic acid, in which it was readily soluble, in colourless rhombic plates, m. p. 108—109° (Found: Cl, 58.85.  $C_{12}H_8ON_2Cl_8$  requires Cl, 59.1%).

*The Action of Acetic Anhydride upon  $\alpha\beta$ -Dichlorocrotonaldehyde-2:4-dichlorophenylhydrazone.*—When warmed with acetic anhydride containing a drop of concentrated sulphuric acid, the hydrazone reacted with evolution of heat to give a clear brown solution, from which  $\alpha\beta$ -dichlorocrotonaldehyde-N-acetyl-2:4-dichlorophenylhydrazone separated on cooling. It crystallised from boiling alcohol or acetic acid, in which it was easily soluble, in six-sided prisms, m. p. 122.5° (Found: C, 42.2; H, 3.5; N, 8.5; Cl, 41.6; *M*, cryoscopic in benzene, 329, 333.  $C_{12}H_{10}ON_2Cl_4$  requires C, 42.4; H, 3.0; N, 8.2; Cl, 41.7%; *M*, 340).

*Action of Chlorine upon  $\alpha\beta$ -Dichlorocrotonaldehyde-N-acetyl-2:4-dichlorophenylhydrazone.*—A slow stream of chlorine was passed into a suspension of 2 g. of the acetylhydrazone in 10 c.c. of glacial acetic acid, cooled to prevent any marked rise in temperature. The clear solution obtained was set aside for 4 hours. On cautious

addition of water,  $\alpha\beta\beta$ -tetrachlorobutaldehyde-N-acetyl-2 : 4-dichlorophenylhydrazone separated; this was moderately easily soluble in boiling alcohol, from which it separated in colourless compact prisms, m. p.  $97-98^\circ$  (Found : Cl, 51.7.  $C_{12}H_{10}ON_2Cl_6$  requires Cl, 51.8%).

*The Action of 2 : 4-Dichlorophenylhydrazine Hydrochloride upon Butyl Chloral Hydrate in Ethyl Alcohol : Formation of  $\beta$ -Chloro- $\alpha$ -ketobutaldehyde-2 : 4-dichlorophenylhydrazone (V).*—20 G. of 2 : 4-dichlorophenylhydrazine hydrochloride (1 mol.), 18 g. of butyl chloral hydrate (1 mol.), and 150 c.c. of ethyl alcohol were gently warmed together. As the reactants dissolved, a bright red colour was developed and, when the boiling point of the alcohol was reached, a vigorous reaction set in, hydrogen chloride was freely evolved, and the alcohol continued to boil for some time without further heating. The bright red colour gradually disappeared and the solution became pale yellow.

Half the alcohol was then distilled off and the concentrated solution left to cool; the yellow crystals thus obtained, after being washed with a little cold ligroin, separated from boiling alcohol, in which they readily dissolved, in pale yellow, very slender, hair-like prisms, m. p.  $129^\circ$  (Found : C, 43.2; H, 3.3; N, 10.3; Cl, 38.0.  $C_{10}H_9ON_2Cl_3$  requires C, 42.9; H, 3.3; N, 10.0; Cl, 38.0%).

$\beta$ -Chloro- $\alpha$ -ketobutaldehyde-2 : 4-dichlorophenylhydrazone was also formed when the reaction was carried out in acetic acid solution, the evolution of hydrogen chloride being naturally more marked in this case.

*The Action of Benzoyl Chloride upon  $\beta$ -Chloro- $\alpha$ -ketobutaldehyde-2 : 4-dichlorophenylhydrazone.*—4 G. of benzoyl chloride (1 mol. + excess) were added to 2 g. of the hydrazone dissolved in 6 g. of pyridine. After 30 hours, the deep orange-coloured reaction mixture was poured into dilute hydrochloric acid and the oily layer which separated was washed with aqueous alkali to remove excess of benzoyl chloride. When digested with a few c.c. of warm alcohol, the oil solidified to a mass of crystals.  $\beta$ -Chloro- $\alpha$ -ketobutaldehyde-N-benzoyl-2 : 4-dichlorophenylhydrazone crystallises from boiling alcohol, in which it is sparingly soluble, in small, colourless, compact prisms, m. p.  $166.5^\circ$  (Found : Cl, 28.0.  $C_{17}H_{13}O_2N_2Cl_3$  requires Cl, 27.75%).

*The Interaction of 2 : 4-Dichlorophenylhydrazine Hydrochloride with  $\beta$ -Chloro- $\alpha$ -ketobutaldehyde-2 : 4-dichlorophenylhydrazone in Methyl Alcohol : Formation of  $\alpha$ -Keto- $\beta$ -methoxybutaldehyde-2 : 4-dichlorophenylosazone (VI).*—2 G. (1 mol.) of the hydrazone and 1.5 g. of 2 : 4-dichlorophenylhydrazine hydrochloride (1 mol.) in 20 c.c. of methyl alcohol were boiled for about 5 minutes and cooled. The osazone obtained was readily soluble in boiling pyridine, from which



it separated in compact, bright yellow prisms, m. p.  $196^{\circ}$  (decomp.). It is very sparingly soluble in boiling alcohol, but may be recrystallised from boiling benzene [Found: C, 46.8; H, 3.8; N, 12.9; Cl, 32.95; OMe, by Hewitt and Moore's modification (J., 1902, 84, 318) of Zeisel's method, 7.1.  $C_{16}H_{13}N_4Cl_4(OMe)$  requires C, 47.0; H, 3.7; N, 12.9; Cl, 32.7; OMe, 7.15%].

The corresponding *ethoxy-osazone*, similarly prepared in ethyl-alcoholic solution, crystallised from boiling alcohol, in which it was sparingly soluble, in dull yellow, irregular plates, m. p.  $162^{\circ}$  (decomp.) [Found: Cl, 31.5; OEt, 8.9.  $C_{16}H_{13}N_4Cl_4(OEt)$  requires Cl, 31.65; OEt, 9.95%].

*The Interaction of 2 : 4-Dichlorophenylhydrazine Hydrochloride and Butyl Chloral Hydrate in Methyl Alcohol.*—When a powdered mixture of 20 g. of 2 : 4-dichlorophenylhydrazine hydrochloride (1 mol.) and 18 g. of butyl chloral hydrate (1 mol.) suspended in 50 c.c. of methyl alcohol was treated in the way described for the reaction in ethyl alcohol (p. 92), the same phenomena were observed as in that case; when cold, the reaction mixture had almost solidified to a pulp of crystals. These were separated and extracted with 50 c.c. of boiling ethyl alcohol, a quantity (A) remaining undissolved. The solution, on cooling, deposited yellow needle-like crystals which, after repeated crystallisation from alcohol, melted at  $129^{\circ}$  (8 g.), alone or mixed with  $\beta$ -chloro- $\alpha$ -ketobutaldehyde-2 : 4-dichlorophenylhydrazone (Found: Cl, 37.9. Calc.: Cl, 38.0%).

The material (A), after being extracted twice more with 50 c.c. of boiling ethyl alcohol, left a yellow crystalline residue sparingly soluble in most of the common organic solvents; this separated from boiling pyridine, in which it was moderately easily soluble, in bright yellow, compact prisms (9 g.), m. p.  $196^{\circ}$  (decomp.), identical with the methoxy-osazone described above (Found: Cl, 32.7. Calc.: Cl, 32.7%).

Similar series of reactions were carried out with 2-chloro-4-bromophenylhydrazine and 2 : 4-dibromophenylhydrazine, the following compounds, all crystallised from alcohol, being prepared:—

$\alpha\beta$ -Dichloro- $\alpha\beta$ -dibromobutaldehyde-2 : 4-dibromophenylhydrazone, slender, hair-like, dull yellow prisms, m. p.  $119.5^{\circ}$  (Found: C, 30.7; H, 2.3; N, 7.3; Cl, 18.3; Br, 41.3.  $C_{10}H_8N_2Cl_2Br_2$  requires C, 31.0; H, 2.1; N, 7.2; Cl, 18.3; Br, 41.3%).

$\alpha\beta$ -Dichloro- $\alpha\beta$ -dibromobutaldehyde-2 : 4-dibromophenylhydrazone, colourless compact prisms, m. p.  $132$ — $133^{\circ}$  (decomp.) (Found: Cl, 13.1; Br, 58.7.  $C_{10}H_8N_2Cl_2Br_4$  requires Cl, 13.0; Br, 58.5%).

$\alpha\beta$ -Dichloro- $\alpha\beta$ -dibromobutaldehyde-N-acetyl-2 : 4-dibromophenylhydrazone, colourless, compact, rhombic plates, m. p.  $141^{\circ}$  (Found: Cl, 16.5; Br, 37.3.  $C_{12}H_{10}ON_2Cl_2Br_2$  requires Cl, 16.5; Br, 37.3%).

$\alpha\beta$ -Dichlorocrotonaldehyde-2-chloro-4-bromophenylhydrazone, slender, pale yellow prisms, m. p.  $118^\circ$  (Found: C, 35.2; H, 2.3; N, 8.2; Cl, 31.0; Br, 23.3.  $C_{10}H_8N_2Cl_3Br$  requires C, 35.0; H, 2.35; N, 8.2; Cl, 31.1; Br, 23.3%).

$\alpha\beta$ -Dichlorocrotonaldehyde-N-acetyl-2-chloro-4-bromophenylhydrazone, colourless plates, m. p.  $134^\circ$  (Found: C, 37.8; H, 2.65; N, 7.3; Cl, 27.75; Br, 20.85.  $C_{12}H_{10}ON_2Cl_3Br$  requires C, 37.5; H, 2.6; N, 7.3; Cl, 27.7; Br, 20.8%).

$\beta$ -Chloro- $\alpha$ -ketobutaldehyde-2-chloro-4-bromophenylhydrazone, very slender, lemon-yellow prisms, m. p.  $135^\circ$  (Found: C, 37.1; H, 2.9; N, 8.6; Cl, 21.9; Br, 24.7.  $C_{10}H_9ON_2Cl_2Br$  requires C, 37.05; H, 2.8; N, 8.65; Cl, 21.9; Br, 24.7%).

$\beta$ -Chloro- $\alpha$ -ketobutaldehyde-2:4-dibromophenylhydrazone, very slender, pale yellow prisms, m. p.  $143.5^\circ$  (Found: Cl, 9.7; Br, 43.6.  $C_{10}H_9ON_2ClBr_2$  requires Cl, 9.6; Br, 43.4%).

$\beta$ -Chloro- $\alpha$ -ketobutaldehyde-N-benzoyl-2:4-dibromophenylhydrazone, colourless compact prisms, m. p.  $183.5^\circ$  (Found: Cl, 7.5; Br, 33.75.  $C_{17}H_{13}O_2N_2ClBr_2$  requires Cl, 7.5; Br, 33.8%).

$\alpha$ -Keto- $\beta$ -methoxybutaldehyde-2:4-dibromophenylsazone, bright yellow prisms, m. p.  $194^\circ$  (decomp.), from pyridine or alcohol (Found: C, 33.8; H, 2.8; N, 9.2; Br, 52.3.  $C_{17}H_{16}ON_2Br_2$  requires C, 33.3; H, 2.6; N, 9.2; Br, 52.25%).

$\alpha$ -Keto- $\beta$ -ethoxybutaldehyde-2:4-dibromophenylsazone, yellow, six-sided plates, m. p.  $177^\circ$  (decomp.) (Found: Br, 50.6.  $C_{18}H_{18}ON_2Br_2$  requires Br, 50.8%).

Part of the earlier work described in this paper was carried out in association with Mr. John Cripps Brashaw of Trinity College.

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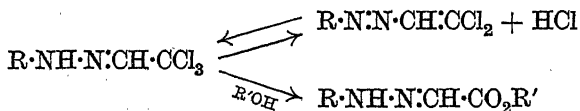
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## XVI.—The Formation of Glyoxalosazones by the Interaction of Dichloroacetaldehyde and Aryl Hydrazines.

By FREDERICK DANIEL CHATTAWAY and LARKIN HUNDLEY  
FARINHOLT.

WHEN chloral reacts with aryl hydrazines (Chattaway and Bennett, J., 1927, 2850; Chattaway and Daldy, J., 1928, 2756), pale yellow hydrazones are first formed. These are extremely unstable and lose hydrogen chloride very easily, brilliant crimson azo-derivatives of  $\alpha\alpha$ -dichloroethylene being obtained. This loss of hydrogen chloride, however, is a reversible reaction and if the acid is not removed and if the reaction is carried out in alcoholic solution, the trichloromethyl group of the original hydrazone is hydrolysed and

a hydrazone of a glyoxylic ester is produced. The equilibrium being thus destroyed, the red colour at first produced disappears as the azo- $\alpha\alpha$ -dichloroethylene reverts to the original hydrazone :



A similar series of reactions occurs when dichloroacetaldehyde reacts with aryl hydrazines. Hydrazones are at first normally produced which quickly lose hydrogen chloride with the production of a brilliant crimson colour.

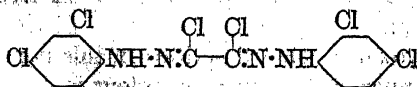
This crimson colour is undoubtedly due to the formation of azo-derivatives of  $\alpha$ -monochloroethylene. These, however, are too unstable to allow of their isolation in a pure state and, the reactions by which they are produced being reversible, the crimson colour rapidly disappears on heating and osazones of glyoxal separate, since the dichloromethyl group of the parent hydrazones is very reactive and condenses with another molecule of the aryl hydrazine, either directly or after hydrolysis : thus, where R is  $\text{C}_6\text{H}_5$ , 4- $\text{C}_6\text{H}_4\text{Cl}(\text{Br})$ , 2 : 4- $\text{C}_6\text{H}_3\text{Cl}_2(\text{Br}_2)$ , or 2 : 4 : 6- $\text{C}_6\text{H}_2\text{Cl}_3(\text{Br}_3)$ ,



In this connexion it may be recalled that  $\alpha\alpha$ -dichloro-5-carboxy-2-hydroxyacetophenone similarly yields an osazone with phenylhydrazine (Chattaway and Calvet, J., 1927, 687).

The glyoxalosazones are pale yellow, well-crystallised compounds, for the most part sparingly soluble in ordinary organic solvents. They melt at a high temperature, usually with decomposition, and are easily chlorinated and brominated. They also form well-crystallised diacetyl derivatives,  $\text{R}\cdot\text{N}\cdot\text{Ac}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{Ac}\cdot\text{R}$ .

The action of chlorine on the unsubstituted glyoxaldiphenylosazone, on glyoxaldi-*p*-chlorophenylosazone, and on glyoxaldi-2 : 4-dichlorophenylosazone yields the same product,  $\omega\omega'$ -dichloroglyoxaldi-2 : 4-dichlorophenylosazone,



Direct halogenation does not introduce a third chlorine atom into the benzene nucleus.  $\omega\omega'$ -Dichloroglyoxaldi-2 : 4 : 6-trichlorophenylosazone, however, is readily formed by the action of chlorine on glyoxaldi-2 : 4 : 6-trichlorophenylosazone.

Bromine acts in an exactly analogous manner, being substituted for hydrogen in the benzene nuclei and replacing the two  $\omega\omega'$ -hydrogen atoms.

The  $\omega\omega'$ -substituted halogen atoms in these compounds are remarkably unreactive. The  $\omega\omega'$ -halogenated osazones can be recovered unchanged even after refluxing with alcoholic ammonia for some hours. They are also not readily reduced by tin or zinc in hydrochloric or acetic acid.

The glyoxalosazones, when the  $\omega\omega'$ -positions are occupied by halogen atoms, are not acetylated when heated with acetic anhydride, tarry products being obtained; nor can chlorine or bromine be substituted for hydrogen in the  $\omega\omega'$ -positions in the diacetylosazones, even on heating in glacial acetic acid for several hours, the initial material being recovered.

#### EXPERIMENTAL.

*Action of Phenylhydrazine upon Dichloroacetaldehyde.*—As the same results were obtained whether dichloroacetaldehyde alcoholate or dichloroacetaldehyde itself was used, the former was always employed, since it is very troublesome to isolate the aldehyde.

To 150 c.c. of acetic acid were added 15.9 g. of dichloroacetaldehyde alcoholate (1 mol.) and 21 g. of phenylhydrazine (2 mols.). On being gently warmed, the solution developed a crimson colour which, as the temperature was raised to about  $70^\circ$ , disappeared and glyoxal-diphenylosazone separated. This compound crystallised from boiling alcohol, in which it was moderately easily soluble, in clusters of pale yellow, rhombic plates, m. p.  $169-171^\circ$  (compare Oddo and Cusmano, *Gazzetta*, 1911, **41**, ii, 251).

*Action of p-Chlorophenylhydrazine Hydrochloride upon Dichloroacetaldehyde Alcoholate.*—To 150 c.c. of acetic acid were added 16 g. of dichloroacetaldehyde alcoholate (1 mol.), 36 g. of p-chlorophenylhydrazine hydrochloride (2 mols.), and 20 g. of anhydrous sodium acetate. On warming, a brilliant crimson colour developed which on further heating disappeared and glyoxaldi-p-chlorophenylosazone separated. It crystallised from boiling alcohol or acetic acid, in both of which it was sparingly soluble, in pale yellow, quadrilateral plates, m. p.  $227^\circ$  (decomp.) (Found: Cl, 22.9.  $C_{14}H_{12}N_4Cl_2$  requires Cl, 23.1%).

The other glyoxalosazones described in this paper were prepared in a similar manner, a deep crimson colour in each case appearing, and disappearing as the heating proceeded and the yellow osazone separated.

*Glyoxaldi-2:4-dichlorophenylosazone* crystallises from boiling acetic acid, in which it is very sparingly soluble, in clusters of pale

yellow needles, m. p. 253—254° (decomp.) (Found: Cl, 37.5; C, 44.8; H, 2.6; N, 14.9.  $C_{14}H_{10}N_4Cl_4$  requires Cl, 37.7; C, 44.7; H, 2.7; N, 14.9%).

*Glyoxaldi-2 : 4 : 6-trichlorophenylosazone* crystallises from acetic acid or alcohol, in both of which it is moderately easily soluble, in clusters of very pale yellow needles, m. p. 189° (Found: Cl, 47.8.  $C_{14}H_8N_4Cl_6$  requires Cl, 47.8%).

*Glyoxaldi-p-bromophenylosazone* separates from either acetic acid or alcohol, in both of which it is sparingly soluble, in pale yellow, quadrilateral plates, m. p. 215° (decomp.) (Found: Br, 40.2.  $C_{14}H_{12}N_4Br_2$  requires Br, 40.4%).

*Glyoxaldi-2 : 4-dibromophenylosazone* crystallises from boiling acetic acid, in which it is very sparingly soluble, in pale yellow, fine needles which darken at about 237° and melt with decomposition at 243° (Found: Br, 57.4.  $C_{14}H_{10}N_4Br_4$  requires Br, 57.7%).

*Glyoxaldi-2 : 4 : 6-tribromophenylosazone* separates from acetic acid, in which it is sparingly soluble, in faintly yellow, quadrilateral plates, m. p. 226—228° (decomp.) (Found: Br, 67.25.  $C_{14}H_8N_4Br_6$  requires Br, 67.4%).

All the glyoxalosazones were easily acetylated when heated with acetic anhydride containing a drop of sulphuric acid. The diacetyl derivatives are all colourless, and were crystallised from acetic acid.

Diacetylglyoxaldiphenylosazone forms quadrilateral plates, m. p. about 360° (decomp.); *diacetylglyoxaldi-p-chlorophenylosazone*, six-sided prisms, m. p. about 330° (decomp.) (Found: Cl, 18.0.  $C_{18}H_{16}O_2N_4Cl_2$  requires Cl, 18.1%); *diacetylglyoxaldi-2 : 4-dichlorophenylosazone*, compact six-sided prisms, m. p. 291—292° (decomp.) (Found: Cl, 30.6.  $C_{18}H_{14}O_2N_4Cl_4$  requires Cl, 30.8%); *diacetylglyoxaldi-2 : 4 : 6-trichlorophenylosazone*, flattened prisms, m. p. about 370° (decomp.) (Found: Cl, 40.0.  $C_{18}H_{12}O_2N_4Cl_6$  requires Cl, 40.2%); *diacetylglyoxaldi-p-bromophenylosazone*, six-sided prisms, m. p. about 340° (decomp.) (Found: Br, 33.4.  $C_{18}H_{16}O_2N_4Br_2$  requires Br, 33.3%); *diacetylglyoxaldi-2 : 4-dichlorophenylosazone*, slender six-sided prisms, m. p. 300° (decomp.) (Found: Br, 50.1.  $C_{18}H_{14}O_2N_4Br_2$  requires Br, 50.1%); and *diacetylglyoxaldi-2 : 4 : 6-tribromophenylosazone*, clusters of needles, m. p. about 365° (decomp.) (Found: Br, 60.3.  $C_{18}H_{12}O_2N_4Br_6$  requires Br, 60.3%).

*Action of Chlorine upon Glyoxaldiphenyl-, Glyoxaldi-p-chlorophenyl-, and Glyoxaldi-2 : 4-dichlorophenylosazones.*—When any one of these osazones was suspended in glacial acetic acid, and a rapid stream of chlorine passed in to saturation, hydrogen chloride was liberated, the suspended osazone dissolved, and *os'-dichloroglyoxaldi-2 : 4-dichlorophenylosazone* separated as a greenish-yellow solid. It crystallised from benzene in pale yellow, fine needles, m. p. 240—

251° (decomp.; after darkening at about 240°) (Found: Cl, 47.6.  $C_{14}H_8N_4Cl_6$  requires Cl, 47.8%).

$\omega\omega'$ -Dichloroglyoxaldi-2:4:6-trichlorophenylosazone was similarly formed by the action of chlorine upon glyoxaldi-2:4:6-trichlorophenylosazone. It is sparingly soluble in boiling acetic acid but much more readily soluble in boiling benzene, from which it crystallises in clusters of very pale yellow, fine needles, m. p. 229—231° (decomp.) (Found: Cl, 55.1.  $C_{14}H_6N_4Cl_8$  requires Cl, 55.2%).

$\omega\omega'$ -Dibromoglyoxaldi-2:4-dibromophenylosazone crystallises from benzene, in which it is moderately easily soluble, in clusters of long, fine, pale yellow needles, m. p. 205° (decomp.) (Found: Br, 67.15.  $C_{14}H_8N_4Br_6$  requires Br, 67.4%);  $\omega\omega'$ -dibromoglyoxaldi-2:4:6-tribromophenylosazone in long, fine, pale yellow needles, m. p. 230° (decomp.) (Found: Br, 73.3.  $C_{14}H_6N_4Br_8$  requires Br, 73.5%);  $\omega\omega'$ -dibromoglyoxaldi-2:4-dichlorophenylosazone in pale yellow needles, m. p. 270—273° (decomp.) (Found: Br, 29.8.  $C_{14}H_8N_4Cl_4Br_2$  requires Br, 29.9%); and  $\omega\omega'$ -dichloroglyoxaldi-2:4:6-tribromophenylosazone in very pale yellow, slender needles, m. p. 257° (decomp.) (Found: Cl, 8.9.  $C_{14}H_6N_4Br_6Cl_2$  requires Cl, 9.1%).  $\omega\omega'$ -Dibromoglyoxaldi-2:4:6-trichlorophenylosazone crystallises from glacial acetic acid in clusters of fine, almost colourless needles, m. p. 246° (decomp.) (Found: Br, 26.8.  $C_{14}H_6N_4Cl_6Br_2$  requires Br, 26.5%).

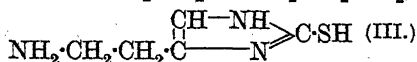
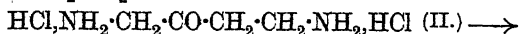
THE QUEEN'S COLLEGE, OXFORD.

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## XVII.—2-Thiol-4(5)- $\beta$ -aminoethylglyoxaline (2-Thiol-histamine).

By FRANK LEE PYMAN.

IN view of the physiological activity of histamine, and of the natural occurrence of ergothioneine, the synthesis of 2-thiolhistamine appeared to be of interest. This has now been effected by using as the starting material,  $\alpha\delta$ -dibenzamido- $\beta$ -ketobutane (I) which Windaus, Dörries, and Jensen (*Ber.*, 1921, 54, 2745) prepared from the tribenzamidobutene resulting from the benzylation of histamine. When  $\alpha\delta$ -dibenzamido- $\beta$ -ketobutane was hydrolysed with



alcoholic hydrochloric acid at 150°,  $\alpha\delta$ -diamino- $\beta$ -ketobutane dihydrochloride (II) was obtained, and on condensation of this with 1 mol.

of sodium thiocyanate 2-thiolhistamine (III) resulted. Its constitution follows from the results of analysis combined with the fact that it yields histamine on oxidation.

Dr. Dale, Sec. R.S., and Mr. J. H. Gaddum, M.A., of the National Institute for Medical Research, to whom the author wishes to express his thanks, found that 50 mg. of 2-thiolhistamine hydrochloride produced a smaller fall in the blood pressure of a cat under ether than 0.001 mg. of histamine when injected intravenously, and also that 50 mg. of 2-thiolhistamine hydrochloride appeared to have no effect upon a 20 g. mouse when injected subcutaneously. Mr. W. A. Broom, B.Sc., of Boots' Pharmacological Department found that 2-thiolhistamine hydrochloride had only one/two-thousandth part of the activity of histamine in causing contraction of the isolated uterus of a virgin guinea-pig, and did not reduce the blood sugar of the rabbit when injected subcutaneously. It appears, therefore, that the substance has no significant histamine-like action.

#### EXPERIMENTAL.

$\alpha\delta$ -Dibenzamido- $\beta$ -ketobutane was prepared by the method of Windaus, Dörries, and Jensen (*loc. cit.*), the yield being 80 to 90% of the theoretical. It melts at 158–159° (corr.) and is not easily soluble in alcohol, requiring about 7 parts by weight of boiling alcohol for solution, and being much less soluble in cold alcohol. Windaus, Dörries, and Jensen give m. p. 151° and state that the substance is easily soluble in alcohol.

$\alpha\delta$ -Diamino- $\beta$ -ketobutane.— $\alpha\delta$ -Dibenzamido- $\beta$ -ketobutane (10 g.), alcohol (50 c.c.), and concentrated hydrochloric acid (50 c.c.) were heated under pressure for 2 hours at 150°. The solution was evaporated to low bulk, extracted with ether to remove benzoic acid, digested with charcoal, filtered, concentrated to low bulk, and mixed with alcohol;  $\alpha\delta$ -diamino- $\beta$ -ketobutane dihydrochloride then crystallised, and further crops were obtained on concentration, the total yield being 73% of the theoretical. This salt crystallises from water in colourless diamond-shaped plates, m. p. 221° (decomp.; corr.). It is anhydrous and is very easily soluble in water, but sparingly soluble in alcohol (Found: C, 27.5; H, 7.4; Cl, 40.3.  $C_4H_{10}ON_2 \cdot 2HCl$  requires C, 27.4; H, 6.9; Cl, 40.5%). On the addition of cold saturated aqueous picric acid it gives a sparingly soluble picrate, crystallising from water in long, yellow, prismatic needles, m. p. 212° (decomp.; corr.).

2-Thiol-4(5)- $\beta$ -aminoethylglyoxaline.— $\alpha\delta$ -Diamino- $\beta$ -ketobutane dihydrochloride (7.0 g.) and sodium thiocyanate (3.24 g.) were dissolved in 20 c.c. of water. The solution was evaporated to a syrup and heated for another hour at 100°, and just enough water was

added to dissolve the sodium chloride which had separated. On keeping, 2-thiolhistamine hydrochloride crystallised; it was purified by recrystallisation from water (yield, 3.7 g. = 52% of the theoretical).

2-Thiol-4(5)- $\beta$ -aminoethylglyoxaline hydrochloride crystallises from water in clusters of colourless prismatic needles, m. p. 248–249° (corr.). It is anhydrous, very easily soluble in water, giving a neutral solution, and almost insoluble in hot absolute alcohol (Found: C, 33.0; H, 6.1; Cl, 19.8; S, 17.9.  $C_5H_9N_3S \cdot HCl$  requires C, 33.4; H, 5.6; Cl, 19.8; S, 17.8%). When cold aqueous solutions of this salt and picric acid are mixed, no immediate precipitate is formed, but a picrate crystallises on keeping in dense, golden, bevelled tablets, m. p. 225° (decomp.; corr.). Aqueous solutions of the hydrochloride give with diazobenzene-*p*-sulphonic acid (a) in the presence of sodium carbonate, an orange colour; (b) under Hunter's conditions (*Biochem. J.*, 1928, 22, 4), in the presence of sodium carbonate and acetate, a yellow solution, which changes to red with a faint purple fluorescence on addition of sodium hydroxide.

*Oxidation.* 2-Thiolhistamine hydrochloride (0.18 g.) was boiled with hydrated ferric chloride (1.6 g.) in water (30 c.c.) for  $\frac{1}{2}$  hour. The solution was partly neutralised with sodium carbonate, mixed with a hot saturated aqueous solution of picric acid (0.46 g.), filtered, and kept. Histamine dipicrate (0.38 g.; yield, 67%) then separated in a pure state, having m. p. 238° (decomp.; corr.) when heated quickly, alone or mixed with an authentic specimen.

RESEARCH LABORATORIES, MESSRS. BOOTS PURE DRUG CO., LTD.,

NOTTINGHAM.

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### XVIII.—Comparison of Some Physical Constants of Thiocyanate, Azide, and Nitrite Solutions.

By P. GÜNTHER and W. PERSCHKE.

CRANSTON and LIVINGSTONE recently published measurements of physical constants of azide and cyanate solutions which led them to infer that the two anions have the same spatial structure in solution (*J.*, 1926, 501). About the same time, the X-ray investigations of Hendricks and Pauling (*J. Amer. Chem. Soc.*, 1925, 47, 2904) definitely proved that in the crystalline state both these ions consist of atoms arranged in an open chain with very similar spacings, as theoretical considerations had first caused Langmuir (*ibid.*, 1919, 41, 1543) to assume, discarding the old ring formula for the azides.

The correspondence of Cranston and Livingstone's conclusions with these results was probably fortuitous. The physical



characteristics of ionic solutions are in general greatly influenced by solvation of the ions, although this may in turn be dependent on the configuration of the atoms in the ion. It is nevertheless certain that considerable differences between ions can be concealed to a great extent by addition of water molecules. Yet if Cranston and Livingstone's conclusions were right in the case of the azide and cyanate ions, in that similarity in the configuration of the ions may be inferred from similarity in certain physical properties, we should be in possession of a very simple and convenient method for determining the structure of the thiocyanate ion also.

The following reasons may be given for doubting the validity of Cranston and Livingstone's deductions. In view of the fact that the cyanate is readily decomposed by water, a mixture of water and alcohol was employed as a solvent in determining the density and the refractive index. It would thus appear possible that the various ions would show preference in combining with one species of the molecules of the solvent. Moreover, the experiments only extended in the case of the potassium salts to 0.5*N*-solutions, and in the case of the sodium salts to 1.0*N*-solutions, whereas it is just the high concentrations that are of advantage in discovering the differences in the influence exerted by the solute on the character of the solutions.

In view of the possibility of determining the structure of the thiocyanate ion, we have tested the method employed by Cranston and Livingstone by comparing the physical properties of nitrite solutions with those of azide solutions. The nitrite ion differs little from the azide ion in weight, but in the configuration of its atoms it is certainly quite different, for its structure is very probably similar to that of the nitrate ion, which is known—at any rate in the crystalline state—not to have the nitrogen atom placed in a straight line between two oxygen atoms. We should thus expect nitrite solutions to have physical constants very different from those of azide solutions. With some degree of probability the following surmise can be made as to the difference between the structure of the thiocyanate and the cyanate ion, the latter of which is known to be the same as that of the azide ion, at least in the crystalline state. According to the measurements of Hendricks and Pauling, in the potassium cyanate crystal the centres of gravity of the atoms at the two ends of the cyanate chain are 2.32 Å.U. apart; whereas in the potassium azide crystal the corresponding distance between the two extreme nitrogen atoms is 2.34 Å.U. If we calculate the lengths of the cyanate and azide chains from the radii of the nitrogen, oxygen, and carbon atoms, as determined by Goldschmidt from other crystalline compounds of these elements

("Geochemische Verteilungssätze der Elemente," VII, Die Gesetze der Krystallochemie, Oslo, 1926, pp. 26 *et seq.*), we find the length corresponding to the azide chain to be 2.84 Å.U., and in the case of the cyanate chain 2.85 Å.U. The radii of the atoms in the configurations in question are therefore smaller than usual, but the contraction is practically the same in both cases. Computing the length of the thiocyanate chain in the same way, using Goldschmidt's atomic radius of sulphur (1.04 Å.U.), we find 3.2 Å.U., a value some 18% greater than for the cyanate chain. If, on account of the equal contractions in the case of the azide and cyanate ions, we assume the same contraction to take place in the thiocyanate ion, the ratio of the chain lengths above computed would be more or less preserved.

The molecular weights of sodium azide and sodium thiocyanate are 65.0 and 81.1 respectively. Their influence on the density differences of solutions can be calculated for all concentrations.

In our experiments with sodium azide, thiocyanate, and nitrite we were able to work with pure water as solvent and to attain much higher concentrations than the above-named authors. The experiments show that the correct results which Cranston and Livingstone's method gave are hardly more than accidental. No conclusions can be drawn as to the similarity or dissimilarity of the atomic structure of the ions we investigated. We did not compare the densities of the solids, since, according to the crystallographic determination of Hendricks and Pauling, it is hardly possible that sodium thiocyanate can have the same arrangement of ions in the crystal as potassium cyanate; so we left out this comparison, carried out by Cranston and Livingstone, but we introduced another series of experiments, comparing the viscosities of the solutions.

#### EXPERIMENTAL.

*Materials.*—Sodium azide was recrystallised from water by precipitation with alcohol and sodium thiocyanate was recrystallised from alcohol. The sodium nitrite was Kahlbaum-Schering's "purissimum." The purity of the azide was determined by precipitation as silver azide, which was converted into chloride and weighed as such, the analysis being checked by decomposing the azide with titrated sulphuric acid: the percentage varied between 97.0 and 98.2%. The sodium nitrite contained 97.8% of pure salt, and the thiocyanate 98%, as determined by titration with silver nitrate. Impurities certainly had no influence on the validity of the conclusions drawn from the experiments. 3*N*-Solutions of these salts were prepared, and diluted with distilled water as required.

*Densities.*—The following densities were determined with Mohr's specific gravity scales and, in part, checked with a pycnometer.

*Densities of aqueous solutions at 20.1°.*

	<i>M</i> =	3.0.	2.0.	1.0.	0.5.	0.25 (at 16.7°).
NaN <sub>3</sub> .....	1.1137	1.0764	1.0380	1.0184	1.0099	
NaCNS .....	1.1162	1.0786	1.0395	1.0198	1.0101	
NaNO <sub>2</sub> .....	1.1273	1.0857	1.0427	1.0210	—	

The densities of the azide and thiocyanate solutions differ very slightly—by less than 0.3% in the highest concentrations. The influence of the greater molecular weight of the thiocyanate is almost completely compensated for by the marked contraction taking place on dissolution, which amounts to as much as 3.85%. In comparing the azide with the nitrite solutions a discrepancy is observable, which can, however, be ascribed chiefly to the greater molecular weight of the latter substance; it is therefore impossible to draw any conclusions from these observations as to the configuration of the ions.

*Viscosity.*—The viscosities were determined with an Ostwald viscometer :

*Coefficients of viscosity at 20.1° (water = 1).*

	<i>M</i> =	3.0.	2.0.	1.0.	0.5.
NaN <sub>3</sub> .....	1.344	1.179	1.050	1.006	
NaCNS .....	1.254	1.105	1.043	1.005	
NaNO <sub>2</sub> .....	1.281	1.126	1.046	1.006	

Corresponding to differences in the contraction occurring in solution, the azide ion has the greatest influence on the viscosity coefficient and the thiocyanate ion the smallest.

*Refractive Indices.*—The refractive indices were obtained with a Pulfrich refractometer. On account of the differences in density of the solutions, however, it was necessary to compare the values of the specific refractivity, *R*, and for this purpose the densities were redetermined at 25°.

	<i>M</i> =	3.	2.	1.	0.5.
NaCNS .....	1.3831 <sub>9</sub>	1.3669 <sub>9</sub>	1.3500 <sub>2</sub>	1.3413 <sub>1</sub>	
NaN <sub>3</sub> .....	1.3669 <sub>0</sub>	1.3560 <sub>7</sub>	1.3442 <sub>8</sub>	1.3385 <sub>8</sub>	
NaNO <sub>2</sub> .....	1.3542 <sub>4</sub>	1.3475 <sub>8</sub>	1.3404 <sub>9</sub>	1.3365 <sub>8</sub>	

$$R = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}$$

	<i>M</i> =	3.	2.	1.	0.5.
NaCNS .....	0.2096	0.2087	0.2074	0.2067	
NaN <sub>3</sub> .....	0.2026	0.2036	0.2049	0.2056	
NaNO <sub>2</sub> .....	0.1930	0.1970	0.2013	0.2036	

The thiocyanate has the greatest and the nitrite ion the smallest influence on the refraction of light.

*Electrical Conductivity.*—The conductivities, which Cranston and Livingstone determined in methyl-alcoholic solution, were measured in a solution of conductivity water. The electrodes consisted of platinised platinum sheet, and in agreement with the results of Briner and Winkler (*J. Chim. physique*, 1923, 20, 201), as against those of Cranston and Livingstone, the platinum coating was found not to decompose the azide solution. The conductivities were unchanged after  $\frac{1}{2}$  hour, 1 hour, and 2 hours, and at the end of a series of experiments no ammonia could be determined in the solution even with the help of Nessler's reagent.

*Molecular conductivities.*

	$M =$	0.5.	0.25.	0.125.	0.063.
NaCNS .....		65.80	75.04	81.92	90.40
NaN <sub>3</sub> .....		65.54	74.84	81.52	90.40
NaNO <sub>2</sub> .....		62.60	72.36	82.88	93.97

The conductivities of thiocyanate and azide agree up to 0.5*M*, even better than those up to 0.1*M* in Cranston and Livingstone's experiments. The conductivity of the nitrite solution differs in magnitude as well as in its dependence on the concentration.

A survey of all the experimental results here given shows that experiments of this kind do not enable us to draw conclusions as to the configuration of atoms in the ion, as Cranston and Livingstone have done.

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### XIX.—*The Inhibition of Chemical Reactions. Part III. The Inhibition by Sulphur of the Atmospheric Oxidation of Benzaldehyde.*

By KENNETH CLAUDE BAILEY.

It has long been known that benzaldehyde is oxidised rapidly by oxygen or by air, and it has been shown that the velocity of oxidation may be greatly reduced by the presence of *very* small traces of "anti-oxygens," *i.e.*, negative catalysts which are themselves oxidisable (see Moureu and Dufraisse, *Chem. and Ind.*, 1928, 47, 819, 848, for a summary of many previous papers); for instance, one part of sulphur in 100,000 parts reduces it to about one-third (*idem, ibid.*, p. 822).

The following additional facts are of importance to the understanding of the present research. (1) The reaction is a chain reaction, in which several thousand molecules are oxidised for each

quantum absorbed, as proved by Bäckström (*J. Amer. Chem. Soc.*, 1927, **49**, 1460; *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927, **6**, 15 and 16), in amplification of Christiansen's theory. (2) In at least some cases of anti-oxygen action the negative catalyst is itself oxidised; this has been clearly proved for the inhibition by alcohols of the oxidation of sodium sulphite (Alyea and Bäckström, *J. Amer. Chem. Soc.*, 1929, **51**, 90). (3) The velocity of oxidation of benzaldehyde is increased by the addition of sand (Reiff, *ibid.*, 1926, **48**, 2893) or pumice (Brunner, *Helv. Chim. Acta*, 1927, **10**, 707). (4) The reaction certainly takes place in stages (Bäckström, *loc. cit.*), and is retarded by intensive drying (Reiff, *loc. cit.*). It has recently been suggested that pure benzaldehyde does not undergo oxidation (Kuhn and Meyer, *Naturwiss.*, 1928, **16**, 1028). (5) Benzoic acid, produced in the reaction, itself acts as a feeble inhibitor.

Most theories of anti-oxygenic action suppose that the negative catalyst detaches oxygen from its preliminary loose combination with the autoxidisable substance (*e.g.*, benzaldehyde), although there is a difference of opinion as to whether the oxygen is eventually liberated again as such (Moureu and Dufraisse, *loc. cit.*), or is fixed by reaction with the negative catalyst, as in the experiments of Alyea and Bäckström. In the latter case, inhibition must depend on the fact that the oxidation of the inhibitor is incapable of setting up or carrying on a chain of further oxidations.

The part of the problem which seems to have been least satisfactorily dealt with is that mentioned in the first paragraph. The explanation of the inhibitory effect of such minute traces must depend to a large extent on a demonstration of the site of reaction.

Moureu and Dufraisse (*loc. cit.*) and Bäckström (*loc. cit.*) believe the reaction to take place homogeneously in the liquid phase. The first two authors suggest that, as very few of the benzaldehyde molecules are at a sufficiently high energy level to react with oxygen, it is possible for a small number of inhibitor molecules to deal with these activated molecules, an explanation which demands for the original complex of benzaldehyde and oxygen the ability to survive  $10^5$  collisions (if the inhibitor is present in the proportion of one part in  $10^5$  parts) without further reacting with a benzaldehyde molecule to give stable benzoic acid. Bäckström depends on the high quantum yield of the reaction for an explanation of the efficiency of the negative catalyst.

The alternative is that offered by Reiff (*loc. cit.*) and Brunner (*loc. cit.*), and accepted by Rideal (*Trans. Faraday Soc.*, 1928, **24**, 571—574), *viz.*, that the reaction takes place, or is initiated, at the surface of the containing vessel, and is inhibited by the negative catalyst, adsorbed in high concentration on this surface. That

reactions are sometimes thus initiated and inhibited is unquestionable, a case in point being the inhibition of esterification by alkaline catalysts, investigated by the writer (J., 1928, 1204, 3256).

Reiff showed that the velocity of oxidation of 10 c.c. of benzaldehyde, standing without being shaken, was doubled by the introduction of 10 c.c. of sand, the activity of which in promoting the reaction would then be approximately equal to that of the original surface of the vessel. He further showed that 5 c.c. of benzaldehyde with 5 c.c. of sand absorbed oxygen  $1\frac{1}{2}$  times as quickly as 10 c.c. of benzaldehyde alone, and that 2 c.c. of benzaldehyde and 5 c.c. of sand absorbed oxygen three times as quickly. This latter result Reiff interpreted as showing that here the oxygen had to diffuse through a much thinner layer of benzaldehyde to reach the sand and the oxidation rate therefore increased. The rate was greatly increased by shaking, and this was attributed to the increased rate of diffusion of oxygen to the active solid surface.

These experiments, however, only *prove* that oxidation can take place on the surface of the sand. It is *assumed* that the velocity in the absence of added sand depends on the walls of the container. It seems unlikely that the smooth walls of a 50-c.c. vessel could have an activity comparable with that of 10 c.c. of finely-divided sand, and scepticism on this point is increased by the fact that almost identical speeds of reaction were obtained by Reiff with vessels of silica, Pyrex glass, and soft glass, and with vessels lined with paraffin wax. The use of dust-free benzaldehyde caused no decrease in the rate of oxidation. These experiments suggest that the velocity of reaction is appreciably affected only by the introduction of a *large* amount of extra surface. Experiments on paraffin-lined vessels and on the effect of sand are described later.

Brunner performed experiments in a shaking machine, and showed that the velocity of oxidation was increased in direct proportion to the amount of powdered pumice added. Here too it is assumed that the original reaction, in the absence of pumice, is due to the walls of the vessel.

The possibility that the reaction takes place in the vapour phase is rejected by Moureu and Dufraisse (*Chem. Reviews*, 1926, 3, 134, 129), who believe that crystals of benzoic acid appear on the upper portion of the vessel only where benzaldehyde has first condensed as a liquid. The appearance of the vessel in some experiments which were carried on for several days by the writer does not accord with this, for fine needle crystals were formed which projected for a considerable distance into the gaseous phase. In any event, however, the amount of reaction in the gaseous phase is small and, although estimations of the benzoic acid on the vessel wall above

the surface of the liquid were made in many cases, the amount, even where the reaction had proceeded until all the oxygen had been absorbed, never exceeded 4% of the total benzoic acid formed.

The evidence offered in the present paper tends to show that the choice lies, not between a reaction initiated at the solid-liquid interface and one taking place homogeneously in the liquid phase, but between the latter and a reaction initiated at the liquid-gas interface and capable of being inhibited there by a catalyst adsorbed preferentially at that interface.

#### EXPERIMENTAL.

The investigation concerns mainly the oxidation of benzaldehyde by atmospheric air, when standing quietly in an unshaken vessel. Experiments were made with pure oxygen also, but the results were of the same general type as when air was used.

In these experiments the benzaldehyde, unless otherwise specified, was Kahlbaum's pure material, freshly distilled in an atmosphere of nitrogen, and stored under that gas. The velocity of reaction was followed by noting the absorption of oxygen, and no attempt was made to distinguish between the first stage of the reaction (formation of perbenzoic acid) and the final conversion into benzoic acid. The specimen under examination was placed in a vessel connected to a differential manometer, the other arm of which was attached to a vessel of the same size. By reading the difference in height between the two columns of liquid, volume errors due to small variations of temperature were eliminated. In the earlier experiments (Series I—IV) mercury was used as manometric liquid, but in the remainder greater delicacy was obtained by the use of water, and the benzaldehyde was throughout assumed to be moist. [It has already been shown by Brunner (*loc. cit.*) that small variations in moisture content have little effect on velocity of oxidation.]

*Series I.*—The velocity of oxidation of pure benzaldehyde in plain glass vessels was compared with that in vessels to which had been added solid glass rods whose total geometrical surface was approximately equal to that of the portion of the containing vessel in contact with the liquid. The results were not very consistent. Sometimes the vessel with added surface showed a slightly higher velocity than the other, sometimes slightly lower. In no case was the speed of reaction increased by more than 15%.

*Series II.*—Experiments were carried out with the same amount of pure benzaldehyde in flasks and tubes of different shapes but approximately the same volume. The rate of absorption over a period of 2 hours was roughly proportional to the area of the liquid-gas interface. For example, when this interface was increased in

the ratio 7.8, the velocity increased in the ratio 7.2, and with an area ratio of 3.2 the velocity ratio was 2.6.

*Series III.*—In all vessels the benzaldehyde is drawn up on the glass wall by capillary action to some little height above the liquid surface, and it seemed possible that reaction might be very intense in these places where liquid-gas and liquid-solid interfaces are close together. Experiments were performed in which were introduced glass rods of such a length as to project slightly above the surface of the liquid and thus increase the area of this liquid film. The velocity of reaction was found to be diminished rather than accelerated.

*Series IV.*—When benzaldehyde is shaken in air, the velocity of oxidation is greater than when the liquid stands quietly. It has already been pointed out that shaking increases the diffusion of oxygen to the solid surfaces. It is also true, however, that it increases diffusion into the homogeneous phase, and again, that it increases greatly the area of the liquid-gas interface, which cannot be neglected as a possible site of reaction.

Brunner's experiments, already quoted, employed a relatively enormous increase of surface (pumice). It was desirable to try a surface comparable with that of the original flask. For obvious reasons, it is impossible to agitate violently a glass flask containing a number of loose solid glass rods. An extra surface was therefore added by fixing a spiral of solid glass of known surface area into the stopper of the flask. The flask employed had a capacity of 155 c.c., and a surface area of 130 sq. cm. to the highest point to which the benzaldehyde splashed during shaking at 160 revolutions per min. The solid coil had a surface area, exposed to the shaken benzaldehyde, of 31 sq. cm., or 24% of the area of the original surface. The volume of the coil was 6 c.c., and this was taken into account in calculating the absorption of oxygen.

The experiments A were performed in sunlight at 5°, and B in the dark at 12.4°. The solid coil was omitted in A1 and B1, and included in A2 and B2;  $t$  is the time interval from the start (in minutes) and  $R$  the average rate of absorption of oxygen (c.mm./min.).

$t$ .	$R$ .		$t$ .	$R$ .	
	A1.	A2.		B1.	B2.
0—3	730	640	0—5	445	380
4—6	570	550	6—14	156	154
7—9	530	450	15—24	116	120
10—12	400	410	25—35	114	107
13—15	430	380	36—44	110	107
16—18	330	290	45—56	100	111
19—21	330	320	57—70	114	105
22—24	330	290			
25—27	300	290			
28—30	270	210			
0—30	422	383	0—70	140	135



In experiments A the oxygen consumption declined by 9.2% when extra surface was included, and in B by 3.6%, whereas an increase of about 24% was to be anticipated if the reaction took place solely on the solid surface. Two other pairs of experiments were performed in the dark, at temperatures of 10.5° and 11.0°, and in each case a diminution of speed of about 4% on inclusion of the extra surface was noted.

*Series V.*—In these experiments cylindrical glass bottles of about 330 c.c. capacity and 5.2 cm. diameter were used. In bottle B the circular bottom was almost flat, in A it was slightly convex; otherwise the bottles were similar. A differential water manometer, with a bottle of the same size containing only air saturated with water vapour, was used in each case. In those experiments where it was used, the light was supplied by a single electric bulb. For A, the distance of the bottle from the light was 88 cm., and for B, 44 cm. In all cases there was an initial rapid absorption which declined rapidly to an almost constant rate. The initial absorption was difficult to measure accurately and the irregularities are probably largely due to experimental error. The average rate of absorption over the period 14—104 minutes was taken as the significant rate for each experiment.

Three types of experiment were made with each bottle. In the first, 12 c.c. of benzaldehyde were employed, in the second 12 c.c. of benzaldehyde and eight glass rods (of total surface approximately equivalent to the submerged surface of the containing bottle), and in the third 5 c.c. of benzaldehyde. The temperature of experiment throughout was 15.3°. In most experiments the first reading of the manometer was taken  $\frac{1}{2}$  minute after the benzaldehyde began to be run into the bottle.

*Bottle B. Light at 44 cm.*

Conditions.	(1) 12 c.c. Ph-CHO.		(2) 12 c.c. Ph-CHO + rods.		(3) 5 c.c. Ph-CHO.	
	<i>t.</i>	<i>R.</i>	<i>t.</i>	<i>R.</i>	<i>t.</i>	<i>R.</i>
	$\frac{1}{2}$ —1	345	$\frac{1}{2}$ —1	462	$\frac{1}{2}$ —1	473
	1—3	273	1—3	274	1—3	293
	3—5	208	3—5	228	3—5	211
	5—10	172	5—10	149	5—8	173
	10—14	137	10—14	112	8—14	126
	14—24	120	14—24	109	14—24	92
	24—42	120	24—36	99	24—34	88
	42—62	120	36—47	99	34—43	82
	62—85	114	47—60	106	43—53	85
	85—104	114	60—72	99	53—67	76
			72—91	92	67—78	72
			91—104	89	78—88	63
					88—104	
	14—104	117.2	14—104	98.2	14—104	76.5

A repetition of the above experiments, and experiments under

the same three sets of conditions with B in the dark, and with A in the dark and the light, followed a similar course, and the following summary gives only the steady rates (values of  $R$  for 14—104 mins.).

		Values of $R$ under conditions		
		(1).	(2).	(3).
Bottle B.	Light .....	117.2, 106.7	98.2, 96.8	76.5, 84.3
"	Dark .....	48.0	41.6	48.3
Bottle A.	Light .....	62.7	67.4	55.7
"	Dark .....	40.1	45.7	47.8

These results show that the effect of doubling the solid-liquid interface is small. In A, it results in a slight increase in velocity, and in B in a reduction (a result confirmed in Series IX). The experiments of Reiff and Brunner make it probable that some portion, at least, of the reaction takes place on the solid surface. We may have here the net result of two opposite effects, an acceleration due to an increase in solid surface, and a diminution in velocity explainable in some other way. The fact that, in all experiments performed in the light, the velocity with a shallow layer of benzaldehyde is markedly less than with a deep layer suggests that the diminution in velocity is due to earlier interruption of the reaction chain postulated by Christiansen and Bäckström.

The fact that 5 c.c. of benzaldehyde absorb oxygen more slowly than 12 c.c. in a similar vessel can hardly be due to the greater proportional accumulation of benzoic acid, as the percentage of this acid formed in these experiments is always low and quite insufficient to explain the results. The latter appear to contradict Reiff's experiments in which 2 c.c. of benzaldehyde over 5 c.c. of sand absorbed oxygen twice as quickly as 5 c.c. of benzaldehyde over 5 c.c. of sand. The difference is probably due to the fact that the particular sand used had a much more active, as well as more extensive, surface than the glass vessel, and the acceleration here outweighed the diminution in velocity due to earlier interruption of the reaction chain. On this theory, the fact that addition of extra surface to A results in a small increase in velocity, in contrast to the result in B, may be due to the different distribution of liquid and solid resulting from the slight convexity of the bottom of A. The relative importance of the two opposite effects may, therefore, be different in the two bottles.

*Series VI.*—These experiments were performed with three tubes of 34 c.c. capacity and 1.4 cm. diameter, prepared from uniform soft-glass tubing. One tube (T) was left in its original condition. Another (N) was narrowed slightly, and in the third (W) a small bulb was blown, in positions such that 6 c.c. of benzaldehyde filled the

tube to the centre of the narrowing or the bulb respectively. Allowance being made for the liquid creeping on the glass to the extent of 0.3 cm., the total liquid surfaces in T, N, and W, respectively, were 3.1, 2.5, and 5.9 sq. cm., or in the ratio 1.0 : 0.81 : 1.90. (If the creep surface is neglected the ratio is 1.0 : 0.69 : 2.20.) We have, therefore, three similar vessels, containing the same amounts of air (28 c.c.) and benzaldehyde (6 c.c.), and with almost identical solid surfaces (submerged area = 22 sq. cm.), but differing in the area of the liquid-gas interface.

Experiments with the light at 44 cm., at 15.3°, showed that the relative steady velocities in T, N, and W for the period 14–104 minutes were 1.0, 0.84, and 2.03, or roughly in the ratio of the areas of the liquid-gas interface.

*Series VII.*—It was thought desirable to repeat Reiff's experiments in which contact of benzaldehyde with the glass surface was prevented by coating the glass with paraffin wax. Experiments were made simultaneously with two similar bottles, one of plain glass, the other lined with paraffin wax. After the subsidence of the short initial period of rapid oxidation (14 mins.), the velocity of reaction in the glass vessel remained almost constant for over an hour. The velocity in the wax-lined vessel, which, at the end of the 14 minutes, was little less than that in the glass vessel, fell off continuously.

An examination of Reiff's curves showed that this happened in his experiment also, although to a less extent. As melted paraffin wax and benzaldehyde are freely miscible, it seemed likely that benzaldehyde would dissolve some solid paraffin wax. It was found that benzaldehyde which had been left over-night under nitrogen in contact with paraffin wax at 15° did not oxidise appreciably for at least an hour when placed in contact with air. Paraffin wax is therefore dissolved, and is a remarkably good inhibitor. The wax used melted at 71° and may have dissolved in benzaldehyde more rapidly than that employed by Reiff.

These experiments make it clear that paraffin wax is not a suitable substance for covering the glass walls of the vessel. The possibility was next considered of floating the benzaldehyde on the surface of an inorganic liquid of higher density. Contact with the solid surface would thus be greatly reduced, and the surface of a liquid can hardly present "active points" for heterogeneous catalysis, such as are believed to be present in a solid catalytic surface. Water is not sufficiently dense, and it was found that benzaldehyde which had been left in contact with a concentrated solution of sodium chloride oxidised much less rapidly than normally, having suffered partial inhibition; a concentrated solution of calcium chloride,

however, proved satisfactory, for benzaldehyde which had been thoroughly shaken with it still oxidised almost as rapidly as before.

A glass-stoppered vessel was filled completely with equal volumes of benzaldehyde and calcium chloride solution and shaken vigorously for  $\frac{1}{2}$  hour. Three cylindrical glass bottles of 290 c.c. capacity and 5.8 cm. diameter were connected to the same water manometer. One was used as a control; into the second (A) were put 10 c.c. of the calcium chloride solution, and 10 c.c. of benzaldehyde previously shaken with calcium chloride were carefully floated on top of it; and into the third (B) were put 10 c.c. of the shaken benzaldehyde, in direct contact with the glass.

Allowing for the rise of liquid on the walls due to surface tension, the ratio of glass surface in contact with benzaldehyde in A and B was 1.0 : 3.4. The following results were obtained.

A {t .....	1-1	1-3	3-5	5-7	7-10	10-15	15-25	25-48	48-61	5-61
{R .....	120	135	141	141	126	132	126	123	117	123
B {t .....	2-4	4-5	5-7	7-9	9-12	12-17	17-27	27-50	50-63	5-63
{R .....	84	75	120	120	120	120	126	134	135	132

The velocity of oxidation in A was about 7% less than in B, instead of 70% less, as would be expected if the reaction were entirely initiated at the glass surfaces. It is noteworthy that these experiments are the only ones performed by the author in which the initial rapid absorption, subsiding after the first few minutes, was absent. The explanation of this phenomenon is still far from clear.

Experiments similar to those of Reiff with sand (already quoted) were also performed, but the geometrical surface area of the silver sand used was evaluated. 1,000 Grains of sand weighed 0.0081 g. The density was 2.6, from which it was calculated (on the assumption that the grains were spherical) that 275 grains have a surface area of 1 sq. cm.

The bottles used for the experiment were similar to those employed in Series V, and the area of glass covered by 10 c.c. of benzaldehyde was about 35 sq. cm. The weight of sand having approximately the same surface area is only 0.08 g. The following results (mean of several experiments) were obtained at 12.7°.

	R (14-74 minutes).
10 c.c. Benzaldehyde .....	50
(a) 10 c.c. Benzaldehyde + 0.08 g. sand .....	46.5
(b) 5 c.c. Benzaldehyde + 10 g. sand .....	33
(c) 11 c.c. Benzaldehyde + 10 g. sand .....	54

These results are quite unlike those of Reiff, but resemble closely those of Series V, in that addition of a sand surface comparable in area with that of the original glass (a) has little effect, while reduction

in the depth of liquid (*b*) diminishes the oxidation. When the original depth of liquid is restored (*c*) (1 c.c. of benzaldehyde extra being allowed for soakage between the grains of sand), the velocity is restored to a value only a little faster than the original. The difference between these results and Reiff's is probably due to the fact that his sand had a surface of much greater specific activity than the silver sand used in these experiments.

*Series VIII.*—The following experiments on benzaldehyde which contained sulphur as an inhibitor were made with the light at 44 cm., and with tubes T and W (see Series VI). The temperature was 15.3°. Since in many of the experiments, the reaction velocity did not become constant as quickly as in the experiments with large bottles (Series V), the mean velocity for the period 34—104 minutes was considered the significant velocity. The following is a summary of the results :

Sulphur, parts per 10 <sup>6</sup> .	<i>R</i> (34—104).		Ratio, W/T.	of original. ~		Diminution % for each part of sulphur per 10 <sup>6</sup> .	
	T.	W.		T.	W.	T.	W.
Nil	1.866	3.475	1.86	100	100		
3.3	1.582	2.927	1.85	84.8	84.2	4.61	4.79
10	0.612	1.028	1.68	32.8	29.6	7.76	8.15
20	0.555	0.920	1.66	29.8	26.5	0.30	0.31
100	0.280	0.434	1.55	15.0	12.5	0.19	0.18
1000	0.124	0.124	1.00	6.6	3.6	0.009	0.010

From these results the following facts emerge.

(1) The ratio of velocities in W and T remains fairly constant as long as the amount of inhibitor present is small.

(2) The effect of each part of sulphur per million appears to be less for the first 3.3 parts than for the next 6.7 parts. That this phenomenon is due to adsorption of sulphur on the solid surface is shown by Series IX. Proportionately more of the first sulphur added is removed from solution, for the solid surface probably becomes rapidly saturated with sulphur. This result is the opposite of what would be expected if the reaction were wholly initiated on the solid surface.

(3) The addition of sulphur causes a very rapid diminution in reaction velocity until the velocity has been reduced to about 30% of the original. After that, further addition of sulphur has a much smaller effect. This suggests that about 70% of the reaction takes place in ways readily affected by inhibitors, and about 30% (in vessels of the shape employed) in ways not readily affected.

*Series IX.*—A few experiments were made with tubes W and T, to which had been added glass rods of 10 sq. cm. surface area (about 45% of the submerged surface of the tube) and volume 1.15 c.c. Only 4.85 c.c. of benzaldehyde were used, so that the liquid level

stood at the same points as before. The other conditions were as in Series VIII.

Sulphur, parts per 10 <sup>6</sup> .	<i>R</i> (34—104).		Velocity as % of original.		Diminution % for each part of sulphur per 10 <sup>6</sup> .	
	T.	W.	T.	W.	T.	W.
Nil	1.704	3.135	100	100		
10	1.184	2.246	69.5	71.6	3.05	2.84
20	0.523	0.868	30.7	27.7	3.88	4.39

These results confirm the fact already noted, that the addition of extra glass surface to benzaldehyde containing no inhibitor is accompanied by a reduction rather than an acceleration in velocity. The further reduction due to the addition of 10 parts of sulphur per million parts is only about 30% instead of 70%, as in the case of benzaldehyde containing no extra glass surface, but 20 parts of sulphur cause a total reduction of about 71%, as against 72% in Series VIII. There is here more solid surface for adsorption of inhibitor, and therefore, with small amounts of inhibitor added, the amount of inhibitor actually available is much less than one would expect.

#### *Discussion.*

It is clear from Series II, VI, and VIII that the velocity of oxidation in unshaken vessels is approximately proportional to the area of the liquid-gas interface. This fact could be reconciled with any of the three following theories: (1) that the reaction is initiated at this interface, (2) that we are measuring a diffusion rate, the reaction taking place in the homogeneous phase, (3) that we are measuring a diffusion rate, the reaction taking place at the solid-liquid interface.

Let us first consider theory (3). It is shown in Series I, III, and IX, that addition of extra glass surface is accompanied by no increase in velocity. This can be reconciled with theory (3) only if we assume that the surface of the containing vessel is so catalytically "active" that it is already more than sufficient for all the oxygen that reaches it, and that the addition of extra surface merely means the substitution of new "active points" for some of the original.

The results of Series IV show that we must further assume an ability to cope with the much greater quantity of oxygen which would diffuse to the solid surface when the vessel is shaken at 160 revolutions per minute.

The writer has also performed experiments which show that the velocity of oxidation increases with rate of shaking (and therefore rate of diffusion of oxygen) up to the maximum velocity employed (160 r.p.m.).

The experiment performed in Series VII, with benzaldehyde

floated on calcium chloride solution, seems to prove definitely that the reaction is not, in the main, a solid surface phenomenon, for the glass-benzaldehyde interface in the vessel A is only to be found round the edges of the vessel, and is not likely to be reached at all by most of the molecules of oxygen which diffuse into the benzaldehyde near the centre of the liquid surface.

The experiments with sand in Series VII showed that the substitution for glass of an enormously greater surface of silver sand increases very little the velocity of reaction, and these experiments, as well as those in Series V, indicate that when the solid surface is brought nearer to the oxygen by diminishing the depth of liquid, the result (in experiments in the light) is a diminution of speed rather than an increase.

The sand experiments suggest that the results obtained by Reiff are exceptional and must be due to the fact that the sand used by him acted as a decided positive catalyst. This theory, however, conflicts with the idea that we are measuring a diffusion rate to the glass surface where reaction takes place practically instantaneously, for, if this be the case, the substitution of a more active solid surface can make no appreciable change in velocity.

The results quoted in Series VIII, and discussed in (2) under that series, also militate against a solid-surface theory.

The experiments described in this paper afford no means of discriminating with certainty between a homogeneous reaction in which a minute proportion of inhibitor acts by interrupting a chain which would otherwise be much longer, and a reaction initiated at the liquid surface and checked by an inhibitor adsorbed at this surface in high concentration. There are several points, however, which incline the author towards the view that the latter type of reaction is the more important.

The experiments of Series VIII show that the velocity of oxidation is reduced by 70% by the addition of 10 parts of sulphur per million parts, while the addition of further sulphur has a very much smaller effect on the velocity. If these results are plotted, a curve is obtained very similar to that obtained for the effect of pyridine on the esterification of ethyl alcohol and acetic acid (J., 1928, 1204). In the latter case, the portion of the reaction which is readily affected by small amounts of inhibitor was shown to be a surface reaction, while the portion not readily affected is probably a homogeneous reaction. It is at least possible that the similarity of curve is due to a similarity of cause.

In the second place, the idea that the reaction is largely initiated in the surface layer seems reasonable of itself. The concentration of oxygen in the surface layer is clearly higher than in the body of the

liquid, unless we assume that no reaction takes place until the solid surface is reached, an assumption which the author has given reasons for rejecting.

The higher concentration of oxygen in the surface layer should mean more reaction in that layer, but the percentage of inhibition will not be greater there than elsewhere unless there is a preferential concentration of inhibitor at the liquid-gas interface. This hypothesis is so far untested in this case, but experiments on the problem are projected. The possibility that they may yield positive results is increased by the results of experiments by McBain and Davies (*J. Amer. Chem. Soc.*, 1927, **49**, 2230) and Laing, McBain, and Harrison (*Colloid Symposium Monograph*, 1928, **6**, 63), who have shown that, in the case of aqueous solutions of such diverse substances as *p*-toluidine, camphor, amyl alcohol, and sodium oleate, the surface concentration of the solute is high even in dilute solutions, and that, when the bulk concentration reaches 1–5 g. per litre, a surface layer more than one molecule thick is composed almost entirely of solute molecules.

A theory that the reaction is initiated to a considerable extent at the liquid surface does not necessarily conflict with the belief that the reaction is a chain reaction. It merely modifies it by suggesting that the reaction chain usually begins at the liquid surface, where it is more readily interrupted by an inhibitor concentrated there than when it begins in the homogeneous phase where the concentration of inhibitor is lower. The reduction in velocity when the depth of liquid is reduced (Series V and VII) may be due to earlier interruption of the reaction chain by collision with the solid surface. The diminution of reaction in Series III has probably a similar explanation.

The writer desires to record his indebtedness to the trustees of the J. M. Purser Fund (Trinity College, Dublin) for a grant for the purchase of pure benzaldehyde.

TRINITY COLLEGE, DUBLIN.

[Received, June 25th, 1929.]

## XX.—The Conversion of N-Chloroacetanilide into *p*-Chloroacetanilide by Hydrogen and Chlorine Ions.

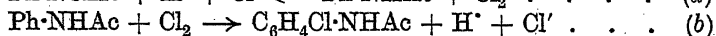
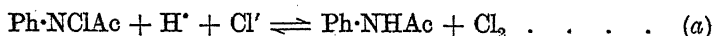
By JOSEPH WATKIN BELTON.

THE theory that the velocity of a chemical reaction in a homogeneous liquid system is determined by the activities of the chemical species concerned has met with some measure of success in certain cases, such as the inversion of sucrose (Jones and Lewis,



J., 1920, 117, 1120; Moran and Lewis, J., 1922, 121, 1613; Scatchard, *J. Amer. Chem. Soc.*, 1923, 45, 1580) and the catalytic decomposition of hydrogen peroxide by bromine-bromide solutions (Livingston and Bray, *ibid.*, p. 2048; Livingston, *ibid.*, 1926, 48, 53). On the other hand, the velocities of some reactions appear to be adequately expressed in terms of the concentrations of the reactants. The velocity of hydrolysis of ethyl acetate catalysed by hydrochloric acid, considered by Harned and Pfanstiel (*ibid.*, 1922, 44, 2194) to be determined by an activity relationship, has recently been found by Dawson and Lowson (J., 1928, 2146) to be proportional to the concentration of the acid over a range 0.0002—0.2*M*, through which the activity coefficient of the hydrogen ion falls by 14%. The velocity of the mutarotation of glucose in water is proportional to the concentration of glucose up to 0.6*M*, and the deviations up to five times this concentration are not great (Hudson and Dale, *J. Amer. Chem. Soc.*, 1917, 39, 320). According to the theory of reaction velocity in solutions developed by Brönsted (*Z. physikal. Chem.*, 1922, 102, 169; 1925, 115, 337), the above conflicting views are special cases of a more general velocity equation which involves the activity coefficients of the reactants and of an intermediate complex. A well-known example of a reaction in which the rate is proportional to the activities of the reactants is the conversion of *N*- into *p*-chloroacetanilide, which occurs in the presence of hydrogen and chlorine ions. It is shown below, however, that the activity theory of reaction rate is of only limited application in this case, and that it breaks down completely when the concentrations of hydrogen and chlorine ions are not equal.

This reaction, which apparently follows a unimolecular course, takes place in two stages (Orton and Jones, *Brit. Ass. Rep.*, 1910, 85):



and only in the presence of both hydrogen and chlorine ions, either ion alone being ineffective. The first stage, being slow compared with the second, determines the velocity of the change. The specific velocity was found by Harned and Seltz (*J. Amer. Chem. Soc.*, 1922, 44, 1476) to be proportional to the product of the activities of the hydrogen and the chlorine ions; at constant temperature their results were satisfactorily represented by the relation

$$K = k_1/a_{\text{H}^+}\cdot a_{\text{Cl}^-} \quad \dots \quad (1)$$

where  $k_1$  is the experimentally determined unimolecular velocity

coefficient,  $a_H$  and  $a_{Cl}$  are the activities of the respective ions, and  $K$  is a constant varying only with temperature. This expression was modified by Soper and Pryde (J., 1927, 2761), who found that better agreement was obtained when the theoretically justified equation

$$K = k_1/a_H \cdot a_{Cl} \cdot f_{NCl} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

was employed,  $f_{NCl}$  being the activity coefficient of the *N*-chloroacetanilide. If the velocity of the change is proportional to the activities of the reacting substances, then we may write

$$v = Ka_H \cdot a_{Cl} \cdot a_{NCl} = Ka_H \cdot a_{Cl} \cdot C_{NCl} f_{NCl}$$

The measured velocity coefficient is given by  $k_1 = v/C_{NCl}$ , and consequently  $K = k_1/a_H \cdot a_{Cl} \cdot f_{NCl}$ . Thus, on this basis the equation employed by Soper and Pryde, rather than that of Harned and Seltz, should be applicable.

In both these investigations the reaction was carried out in the presence of pure hydrochloric acid, in which case the hydrogen- and the chlorine-ion concentrations are necessarily equal. It would appear possible by varying independently the concentration of the two ions, by the addition of acids or of chlorides, to test the applicability of the above equation over a wider range. Measurements of the effect of neutral salts have been made by Rivett (*Z. physikal. Chem.*, 1913, 82, 201; 85, 113), but the concentration terms in which they are expressed render them unsuited for the test of an activity theory of reaction rate. The reaction has therefore been investigated in the presence of mixtures of hydrochloric acid with sodium chloride and with perchloric acid over a wide concentration range.

#### EXPERIMENTAL.

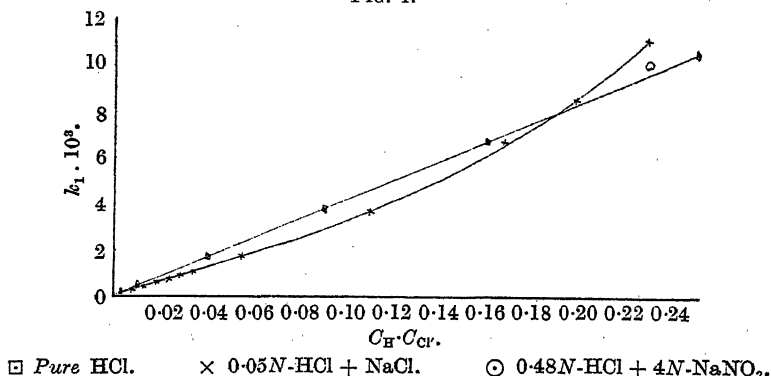
To a solution of *N*-chloroacetanilide, together with the required amount of sodium chloride or perchloric acid, was added the appropriate quantity of pure hydrochloric acid of known strength, both solutions having been first kept for some time at the temperature of reaction—in all cases  $25^\circ (\pm 0.02^\circ)$ . The reaction was then followed iodometrically: at definite times samples were removed and treated with potassium iodide solution and the liberated iodine was titrated with *N*/130-thiosulphate.

A complication is introduced by the *N*-chlorination of the anilides formed (Soper, *J. Physical Chem.*, 1927, 31, 1193), such products reacting with potassium iodide with liberation of iodine. This takes place only to a small extent, and its obviation by the presence of a chlorine acceptor is difficult in salt solutions of high concentration, in which salting-out effects are considerable. Further, in the more

dilute solutions, it was not possible to obtain reproducible results on employing *p*-cresol as such an acceptor. Hydrolysis of the *N*-chloroacetanilide also occurs to a small extent as a side reaction, the result of which is to introduce a small error in a direction opposite to that caused by *N*-chlorination. No attempt has been made here to apply a correction for either of these effects, which tend to annul each other, for it may be shown that the maximum error introduced thereby is of the order of 3%, which is only little greater than the possible experimental error and is too small to invalidate the general conclusions reached.

The velocity coefficients were calculated from the unimolecular equation  $k_1 = 1/t \cdot \log T_1/T_2$ , where  $T_1$  and  $T_2$  are two successive titres and  $t$  is the time interval between them. For each reaction

FIG. 1.



a good constant was obtained. In order to avoid errors due to lack of homogeneity and to increase in temperature on mixing, some time was allowed to elapse between the addition of hydrochloric acid and the initial titration. The specific rate of reaction of *N*-chloroacetanilide and pure hydrochloric acid at 25° was found to be in agreement with the results of Harned and Seltz (*loc. cit.*), whose values have been used in plotting  $K_1$  against  $C_H \cdot C_{Cl}$  for pure hydrochloric acid in Figs 1. and 2.

*Rate of Reaction in Hydrochloric Acid-Sodium Chloride Mixtures.*—The rate of reaction was measured in mixtures in which the concentration of hydrochloric acid was kept approximately constant whilst that of sodium chloride was progressively increased. Table I gives the values of the unimolecular velocity coefficient ( $k_1$ ) in mixtures in which the concentration of hydrochloric acid ( $C_{HCl}$ ) varied only between 0.050 and 0.053*M*, while that of sodium chloride ( $C_{NaCl}$ ) varied from 0.1 to 4.2*M*. Concentrations through-

out are expressed in terms of mols. of solute per 1000 g. of water. The product of the ionic concentrations of hydrogen and chlorine ions ( $C_H \cdot C_{Cl}$ ) is also given, these being calculated on the basis of complete electrolytic dissociation.

TABLE I.

(1)	(2)	(3)	(4)	(5)	(6)	(7)*	(8)*	(9)*
$C_{NaCl}$	$C_{HCl}$	$C_H \cdot C_{Cl}$	$k_1 \cdot 10^4$	$f_{HCl}$	$f_{NCl}$	—	—	—
—	0.05	0.0025	1.25	0.860	—	0.0500	0.0676	—
0.10	0.05	0.0075	3.04	0.804	1.04	0.0405	0.0627	0.0603
0.201	0.0502	0.0126	4.55	0.778	1.08	0.0361	0.0598	0.0554
0.302	0.0504	0.0178	6.05	0.765	1.12	0.0340	0.0582	0.0520
0.404	0.0505	0.0229	7.63	0.759	1.16	0.0333	0.0579	0.0497
0.505	0.0506	0.0281	9.17	0.757	1.21	0.0326	0.0570	0.0471
0.608	0.0507	0.0334	10.8	0.758	1.26	0.0323	0.0563	0.0448
1.021	0.0510	0.0547	17.6	0.785	1.47	0.0322	0.0522	0.0355
2.074	0.0519	0.110	37.0	0.945	2.19	0.0336	0.0376	0.0172
3.152	0.0525	0.168	67.0	1.216	3.25	0.0399	0.0269	0.0083
3.697	0.0528	0.198	85.0	1.402	4.02	0.0429	0.0217	0.0054
4.249	0.0531	0.229	110.0	1.628	4.91	0.0480	0.0182	0.0037

\* Cols. 7, 8, and 9 give the values of  $k_1/C_H \cdot C_{Cl}$ ,  $k_1/C_H \cdot C_{Cl} f_{HCl}^2$ , and  $k_1/C_H \cdot C_{Cl} f_{HCl}^2 f_{NCl}$ , respectively.

In Fig. 1 these values are compared with those obtaining in pure hydrochloric acid solutions. It will be observed that for the latter the velocity coefficient varies linearly with the product  $C_H \cdot C_{Cl}$  over the concentration range employed, while in the presence of increasing sodium chloride concentration, the corresponding curve first lies below and then, at higher concentrations, above that for the pure acid. A similar behaviour is shown in the case of reactions carried out with a higher concentration of hydrochloric acid, again with progressive addition of sodium chloride. The values of the unimolecular velocity coefficients obtained in these reactions are given in Table II, and the relation between them and the product of the concentrations of the hydrogen and chlorine ions is shown in Fig. 2. The curve obtained is similar in general form to that found for mixtures of 0.05*M*-hydrochloric acid with sodium chloride.

TABLE II.

$C_{NaCl}$	$C_{HCl}$	$C_H \cdot C_{Cl}$	$k_1 \cdot 10^3$	$f_{NCl}$	$k_1/C_H \cdot C_{Cl}$	$k_1/C_H \cdot C_{Cl} f_{HCl}^2$
0.499	0.202	0.142	5.03	0.765	0.0354	0.0607
1.007	0.204	0.247	8.47	0.806	0.0343	0.0529
2.110	0.207	0.481	17.2	0.992	0.0358	0.0458
3.244	0.210	0.725	32.7	1.307	0.0451	0.0264

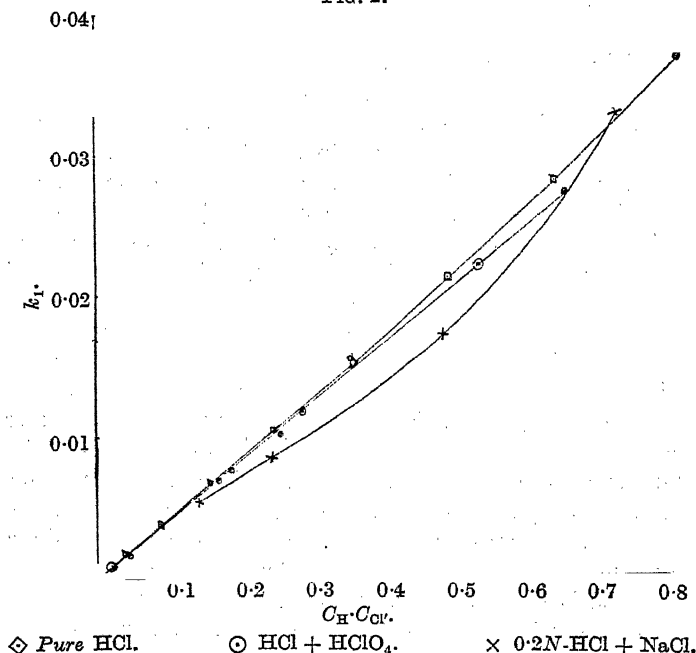
In order to test the applicability of equation (2), *i.e.*, of the simple activity theory of reaction rate, a knowledge is required of the activities of hydrochloric acid and of the activity coefficient of *N*-chloroacetanilide in the systems investigated. The mean activity

coefficients of hydrochloric acid in sodium chloride solutions are given with sufficient accuracy by an equation proposed on empirical grounds by Harned and Brumbaugh (*J. Amer. Chem. Soc.*, 1922, 44, 2729), viz.,

$$\log f_{\text{HCl}} = \alpha c - \beta \mu \alpha' + \alpha''(\mu - c),$$

in which  $\alpha$ ,  $\alpha'$ ,  $\alpha''$ , and  $\beta$  are constants,  $c$  is the molar concentration of hydrochloric acid, and  $\mu$  the ionic strength of the solution. The

FIG. 2.



values of  $f_{\text{HCl}}$  calculated from this expression are given in col. 5 of Table I. The activity of the hydrochloric acid is given by

$$a_{\text{HCl}} = a_{\text{H}} \cdot a_{\text{Cl}} = f_{\text{HCl}}^2 C_{\pm}^2 = f_{\text{HCl}}^2 C_{\text{H}} \cdot C_{\text{Cl}}$$

where  $C_{\pm}$  is the mean molality of the ions.

The activity coefficients of the chloroamide were determined by solubility measurements in sodium chloride solutions of concentrations between 0.1 and 4*M*. The *N*-chloroacetanilide was shaken in a thermostat for some time with a sodium chloride solution of known strength, and a sample rapidly withdrawn through a plug of cotton-wool, by means of a pump. The sample was weighed, and the amount of *N*-chloroacetanilide present estimated iodometric-

ally. From these data its solubility in mols. per 1000 g. of water is calculable. It may be assumed that the presence of 0.05*M*-hydrochloric acid would have but little effect on the solubility in comparison with the concentrations of sodium chloride employed. The activity coefficient of the chloroamide in solution is given by  $m_0/m_s$ , where  $m_0$  is the solubility in pure water, and  $m_s$  that in the salt solution. The activity coefficients found in this way are given in col. 6 of Table I. Incidentally, it may be mentioned that the function,  $\log f_{\text{NCl}}$ , varied linearly with the ionic strength of the solution up to a value  $\mu = 4.3$ .

The numerical values of the expression  $k_1/C_H \cdot C_{\text{Cl}} f_{\text{HCl}}^2$ , given in col. 8 of Table I, are seen to fall throughout with increasing sodium chloride concentration, the value in 4.3*M*-sodium chloride solution being only one-third of that in 0.1*M*-solution. For comparison, the values of  $k_1/C_H \cdot C_{\text{Cl}}$  are given in col. 7. Over the same concentration range, the activity coefficient of the *N*-chloroacetanilide increases from 1.04 to 4.91, and consequently the values of the expression  $k_1/a_H \cdot a_{\text{Cl}} f_{\text{NCl}}$  (col. 9) fall still more rapidly than those of (1). If the velocity of reaction were proportional to the activities of the reacting substances, this expression should be constant at constant temperature; hence the simple activity theory does not apply when sodium chloride is present. A similar divergence is found in the case of more concentrated hydrochloric acid solutions. The values of  $k_1/C_H \cdot C_{\text{Cl}} f_{\text{HCl}}^2$  fall rapidly, and although no numerical data are available, on account of the difficulties involved in the determination of solubilities in hydrochloric acid-sodium chloride mixtures, the activity coefficients of the chloroamide in such solutions would doubtless increase and produce a still greater decrease in the value of expression (2) than in that of (1).

On the basis of Brönsted's theory of the velocity of chemical reactions in solutions, the formation of a critical complex between hydrogen ions, chlorine ions, and chloroamide might be assumed. This would give for the velocity of reaction

$$v = KC_H \cdot C_{\text{Cl}} C_{\text{NCl}} f_H \cdot f_{\text{Cl}} f_{\text{NCl}} / f_{\text{NCl, HCl}} \quad \dots \quad (3)$$

where  $f_{\text{NCl, HCl}}$  is the activity coefficient of the critical complex. If it be assumed that this magnitude varies with the ionic strength of the solution in the same way as does  $f_{\text{NCl}}$ , this expression becomes

$$v = KC_H \cdot C_{\text{Cl}} C_{\text{NCl}} f_H \cdot f_{\text{Cl}} = K a_H \cdot a_{\text{Cl}} C_{\text{NCl}}$$

according to which expression (1) should be constant, but this has been found not to be the case. The numerical values of the terms in equation (3) are known, with the exception of the activity coefficient of the complex. The value of  $f_{\text{NCl, HCl}}/K$  is thus calculable, and is found to increase 16-fold over the concentration range

of Table I. Up to a concentration of 1*M*-sodium chloride, however, this increase is 70%, which might be regarded as a possible (although abnormal) increase for the activity coefficient, but it is found that its logarithm does not bear a linear relation to the ionic strength of the solution, as was found to be the case for *N*-chloroacetanilide itself. A further possibility is the formation of a singly charged complex between the chloroamide and either hydrogen or chlorine ions. This leads to an expression for the velocity  $v = KC_H \cdot C_{\text{NCl}} f_{\text{H}^+} f_{\text{NCl}} / f_{\text{NCl} \cdot \text{H}^+}$ , but this does not lead to a constant value of *K* if similar variation of the activity coefficients of the positively charged ions is assumed. A similar result is obtained if Cl' is substituted for H' in the above equation. It therefore appears to be impossible to formulate an expression, based on the formation of a critical complex by the reactants, which shall agree with the experimental results.

A comparison of the curves obtained with mixtures of hydrochloric acid and sodium chloride, and those of hydrochloric acid alone or with perchloric acid (described below) indicates that the sodium ion exerts some effect on the rate of reaction. In this connexion it is of interest to consider the effect of neutral salts not containing chlorine ions on the velocity coefficient. It was found that with 0.05*M*-hydrochloric acid, the addition of 4*M*-sodium nitrate produced no sensible increase in the value of  $k_1$ , but that with 0.48*M*-acid and 4*M*-nitrate ( $C_H \cdot C_{\text{Cl}'} = 0.23$ ) a slight increase in rate resulted. The latter point is plotted in Fig. 1. This behaviour might be expected if the reaction were of Brönsted's Type 0, in which little salt action is found. The action of sodium chloride is to produce first a slight negative, and then a positive salt effect, and in one case of the reaction types described by Brönsted (*loc. cit.*), the kinetic activity factor (*F*) possesses a value first less and then greater than unity (Type 1.1). This, however, involves the formation of a doubly charged complex, but it would appear difficult to formulate a mechanism of the reaction on this basis.

*The Rate of Reaction in Hydrochloric-Perchloric Acid Mixtures.*—In the experiments described above, the concentration of the chlorine ion was varied over a wide range in comparison with that of the hydrogen ion. By the addition of perchloric acid, which may be regarded as completely dissociated in solution, the concentration of the hydrogen ion may be made much greater than that of the chlorine ion. The experimental procedure was identical with that for sodium chloride solutions. In each case a good unimolecular velocity coefficient was obtained and these are given in Table III together with the corresponding concentration data.

TABLE III.

$C_{HCl}$	$C_{HClO_4}$	$C_H \cdot C_{Cl}$	$k_1 \cdot 10^4$	$C_{HCl}$	$C_{HClO_4}$	$C_H \cdot C_{Cl}$	$k_1 \cdot 10^4$
0.05	0.0935	0.0072	3.2	0.404	0.0570	0.187	76.4
0.051	0.201	0.0132	5.3	0.408	0.217	0.255	101.2
0.101	0.0713	0.0173	7.3	0.410	0.297	0.289	117.0
0.051	0.347	0.0203	7.8	0.423	0.836	0.533	220.0
0.052	0.792	0.0442	16.6	0.429	1.093	0.653	270.0
0.404	0.0187	0.171	69.5				

The relation between the specific velocity of reaction and the product of the ionic concentrations is given in Fig. 2. It shows that within the range investigated (up to  $C_H \cdot C_{Cl} = 0.65$ ), the unimolecular velocity coefficient varies linearly with the product of the molal concentrations of the hydrogen and chlorine ions. The velocity would then be represented by  $v = KC_H \cdot C_{Cl} \cdot C_{NCl}$ . There appears, then, to be no need to introduce the activity theory of reaction rate in this case, the velocity of reaction being proportional to the concentrations of the reacting substances. This result would be in agreement with Brönsted's theory of reaction velocity only if the kinetic activity factor ( $F$ ) showed no variation over the concentration range considered, but it is probable that the activity coefficient,  $f_0$ , of an uncharged molecule would decrease by about 12% in an acid solution of  $\mu = 1.5$ .

### Summary.

The rate of conversion of *N*- into *p*-chloroacetanilide in the presence of (1) hydrochloric acid-sodium chloride and (2) hydrochloric acid-perchloric acid mixtures has been measured over a wide concentration range.

In series (1) the specific rate bears no relation to the activities of the reactants, showing that the activity theory of reaction rate is only of very limited applicability to this reaction. Reaction mechanisms involving the formation of a charged complex, according to the views of Brönsted, also gave no agreement with the experimental data. In mixtures of series (2) the specific rate is proportional to the molal concentrations of hydrogen and of chlorine ions.

In conclusion, the author wishes to express his thanks to Professor H. M. Dawson for the facilities that made the work possible, and for his interest in it during its course.



# XXI.--The Unsaturation and Tautomeric Mobility of Heterocyclic Compounds. Part I. Benzthiazole and Dihydrobenzthiazole Derivatives.

By ROBERT FERGUS HUNTER.

THE objects of this series of investigations are: to study the chemistry of the azole bromides, to compare the mobility of symmetrical and unsymmetrical semicyclic triad systems, and to correlate the additive properties of such heterocyclic derivatives with their behaviour as tautomeric substances.

Benzthiazole was chosen as the starting point of the investigation. According to the conditions of bromination it gave rise either to a well-defined *dibromide* or to an unstable *tetrabromide*, to which the formulæ (I) and (II) respectively are assigned on the following grounds.

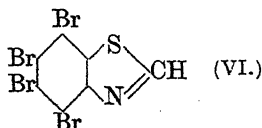
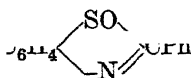
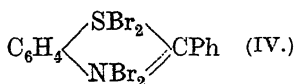
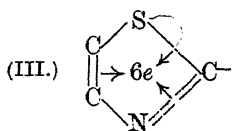


(i) The colour, thermal dissociation, and the ease with which the compounds regenerate the original base on treatment with sulphurous acid, hydriodic acid, ammonia, and similar reagents show that they are additive compounds. (ii) The inability of thiophen to give rise to anything in the nature of an additive complex with bromine under the mildest conditions, the existence of pyridine tetrabromide (Trowbridge, *J. Amer. Chem. Soc.*, 1897, **19**, 558), and the preparation of quinoline tetrabromide (Grimaux, *Bull. Soc. chim.*, 1882, **38**, 124) in a condition of reasonable purity (p. 132) indicate that the nuclear nitrogen atom is the seat of unsaturation in the thiazole ring.

Regarding the electronic formulation of such compounds, it is suggested, since the fifth nitrogen valency is always an electrovalency, that the labile bromine atoms in the dibromide (I) are held by the nuclear nitrogen atom by means of semipolar single bonds, after the manner in which the labile chlorine atoms in phosphorus pentachloride are supposed to be held by the phosphorus atom (Prideaux, *Chem. and Ind.*, 1923, **42**, 672; Ingold and Ingold, *J.*, 1926, 1315; Sugden, *J.*, 1927, 1176). On such a basis, the elimination of  $\text{Br}_2$  in preference to  $\text{Br}^-$  ion from the higher compounds and the facility with which many of the compounds, such as 1-amino-benzthiazole dibromide, pass into the hydrobromides of the corresponding 5-bromo-substituted bases (reversion to ammonium-ion structure) are readily accounted for. The inhibitory effect of the nitro-group on the formation of such compounds (Hunter, *J.*, 1926, 538) also becomes explicable, since the positive end of the semi-

polar double bond,  $\bar{O}=\ddot{N}\cdot\overset{+}{C}$ , would tend to attract electrons from all parts of the molecule.

The formation of a tetrabromide (II) by a repetition of the process of singlet sharing is not difficult to visualise, but there is, however, the possibility that the second pair of labile electrons of the nuclear sulphur atom which are not required for the formation of the sextuple group (III) (Armit and Robinson, J., 1925, **127**, 1605; Goss and Ingold, J., 1928, 1268) might become sufficiently activated, under certain conditions, to give rise to a tetrabromide of the type (IV). On the other hand, the inability of stable tetrabromides, such as 1-phenylbenzthiazole tetrabromide, to yield sulphoxides of the type (V) is strong evidence in favour of the formula (II).



The bromides of benzthiazole present a direct anomaly to all the other compounds of the series in their conversion into a *tetrabromobenzthiazole* under the influence of hydroxylic solvents.

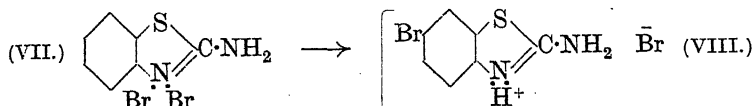
The lack of reactivity of the halogen atoms in this tetrabromocompound in contrast to the behaviour of 1-chlorobenzthiazole towards hydroxylic and reducing agents (Hofmann, *Ber.*, 1879, **12**, 1126; 1880, **13**, 11) appears sufficient evidence for assigning the formula (VI) to the compound. The formation of a similar compound by quinoline (Claus and Istel, *Ber.*, 1882, **15**, 820) emphasises the close relationship existing between benzthiazole and quinoline derivatives.

The tautomeric mobility and the behaviour towards bromine of benzthiazole derivatives containing the triad systems  $[H]N\cdot C:N \rightleftharpoons N:C[N]H$ ,  $[H]N\cdot C:O \rightleftharpoons N:C[O]H$ , and  $[H]N\cdot C:S \rightleftharpoons N:C[S]H$  were next studied.

*1-Aminobenzthiazole*.—The mobility of the symmetrical triad system in 1-aminobenzthiazole has already been established by evidence of the symmetry and substitution type (Hunter, J., 1926, 1385; Hunter and Styles, J., 1928, 3019).

On treatment with a molecular equivalent of bromine at a low temperature, 1-aminobenzthiazole yielded a labile *dibromide* (VII), which, on exposure to air, or when the temperature of the solution

was allowed to rise, was quantitatively converted into the *hydrobromide* of 5-bromo-1-aminobenzthiazole (VIII).



The facility with which the transformation takes place suggests that the mechanism may involve a para-bridged form of 1-aminobenzthiazole, analogous to the formula which Shearer (*Proc. Physical Soc.*, 1923, **35**, ii, 81) has suggested for naphthalene on the basis of X-ray analysis (compare Hunter, J., 1926, 1390; Ingold, J., 1923, **123**, 2081).

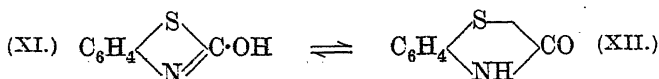
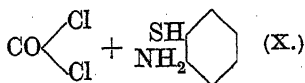
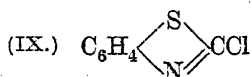
In the presence of excess of bromine, 1-aminobenzthiazole gave rise to an unstable *tetrabromide*, which resembled the dibromide in the ease with which it was converted into 5-bromo-1-aminobenzthiazole hydrobromide.

In the course of these experiments, the bromination of phenylthiocarbamide in chloroform was reinvestigated. The "dibromide of 1-aminobenzthiazole" obtained in this reaction (Hunter, J., 1926, 1389) and described by Huguershoff (*Ber.*, 1901, **34**, 3130) as a bromocarbaminophenylbromoaminodisulphide is actually a *hydrodibromide* of 1-aminobenzthiazole, which can readily be obtained from solutions of the hydrobromide of the amino-base and bromine in inert solvents.

The constitution of this hydrodibromide is a question of considerable importance. In the first place, it is desired to emphasise that the substance is a definite compound and that it is not a eutectic mixture of the hydrobromide of 1-aminobenzthiazole and a hypothetical hydrotribromide. It crystallises from solutions of different concentrations of the components (above a certain minimum concentration of bromine) in inert solvents, and all attempts to prepare the hypothetical hydrotribromide by employing a considerable excess of bromine have failed. Moreover, the remarkable stability of the substance (p. 134) does not appear to be capable of interpretation on the basis of the "physical mixture" type of explanation. It is therefore suggested that the compound may have a structure of the type  $(\text{Base}, \text{H})^+\text{Br}_2^-$ , containing the hitherto unknown  $\text{Br}_2^-$  ion, and involving the operation of a lone singlet linkage.\*

\* Similar corrections must be applied to all the even-numbered bromides obtained from arylthiocarbamides described in earlier papers (Hunter, J., 1925, **127**, 2023, 2270; 1926, 1385, 1401, 2951; Hunter and Soyka, *ibid.*, p. 2958; Dyson, Hunter, and Soyka, *ibid.*, p. 2964; Dyson, Hunter, and

*Mobility and Bromination of 1-Hydroxybenzthiazole.*—The mobility of 1-hydroxybenzthiazole was investigated in a manner similar to that of 1-aminobenzthiazole (*loc. cit.*). 1-Hydroxybenzthiazole (XI), prepared by hydrolysis of 1-chlorobenzthiazole (Hofmann, *Ber.*, 1879, 12, 1126) (IX), was shown to be identical with the ketodihydrobenzthiazole (XII) obtained by treating *o*-aminophenylmercaptan with carbonyl chloride. The low-melting ketodihydrobenzthiazole described by Claasz (*Ber.*, 1912, 45, 1029; compare also Mills and Whitworth, *J.*, 1927, 2752) was shown to be impure 1-hydroxybenzthiazole.



On methylation with methyl sulphate in the presence of potassium hydroxide, however, 1-hydroxybenzthiazole yielded exclusively 1-keto-2-methyl-1 : 2-dihydrobenzthiazole (Besthorn, *Ber.*, 1910, 43, 1523), no trace of the isomeric *O*-methyl derivative being isolable.

On bromination in chloroform at a low temperature, 1-hydroxybenzthiazole yielded a highly unstable bromo-addition compound which immediately lost hydrogen bromide with the production of 5-bromo-1-hydroxybenzthiazole (XVI), whose constitution was established by its synthesis from *p*-bromophenylthiourethane (XIII) by

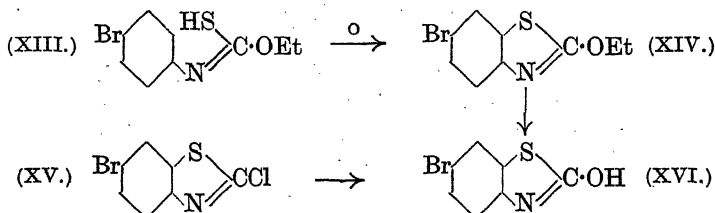
Morris, *J.*, 1927, 1186; Hunter and Styles, *ibid.*, p. 1209; *J.*, 1928, 3019; Hunter and Pride, *J.*, 1929, 943). These compounds are all *hydroperbromides* and are quite distinct from the *true* bromides obtained from the bases themselves, from which they frequently differ in composition only by a hydrogen atom which cannot be detected by analysis. The formula (I) assigned to Huguershoff's 1-anilinobenzthiazole tetrabromide (*Ber.*, 1903, 36, 3121) and to similar compounds (Hunter, *J.*, 1925, 127, 2024) is incorrect. The supposed bimeric tribromides (II) (*loc. cit.*) are hydrotribromides of the type (Base, H)  $\overset{+}{Br_3} \overset{-}{Br_3}$ .



Similar remarks apply to the supposed hexabromides (*J.*, 1925, 127, 2024, 2270, etc.).

The increase of stability in a homologous series of 1-alkylaminobenzthiazole bromides (*J.*, 1926, 2951) can no longer be regarded as due to an enhancement of tautomeric equilibrium in favour of the alkylamino-phase with increase in the atomic volume of the alkyl group.

way of 5-bromo-1-ethoxybenzthiazole (XIV), and also by its formation in the hydrolysis of 1-chloro-5-bromobenzthiazole (XV).



*Mobility and Bromination of 1-Thiolbenzthiazole.*—1-Thio-1:2-dihydrobenzthiazole (XVIII) obtained from thiocarbonyl chloride and *o*-aminophenylmercaptan proved to be identical with 1-thiolbenzthiazole (XVII), prepared from carbon disulphide and *o*-aminophenylmercaptan, whose identity with the mercaptan obtained from 1-chlorobenzthiazole and potassium hydrosulphide was established by Hofmann in 1887 (*Ber.*, 20, 1788) (XVII and XVIII are XI and XII respectively with S in place of O).

Methylation of 1-thiolbenzthiazole, however, yielded the *S*-methyl derivative (XIX), unaccompanied by the isomeric thiomethyldihydrobenzthiazole (XX).



Bromination of 1-thiolbenzthiazole gave rise to a tetrabromo-addition compound, which yielded solely benzthiazolyl 1:1-disulphide on reduction with sulphurous acid.

*Bromination of 1-Phenylbenzthiazole, -selenazole, and -oxazole.*

The bromination of 1-phenylbenzthiazole and of its selenium analogue gave rise to closely similar tetrabromides\* (compare Fromm and Martin, *Annalen*, 1913, 401, 178).

On the other hand, 1-phenylbenzoxazole yielded an unstable hexabromide, which rapidly lost bromine, giving a stable hydrotribromide of 5(?) -bromo-1-phenylbenzoxazole.

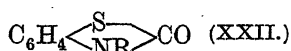
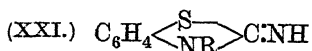
*1:2-Dihydrobenzthiazole Derivatives.*—Reduction of the double

\* Some years ago, 1-phenylbenzthiazole tetrabromide was accidentally isolated in two forms, m. p. 126° and 153° respectively (*J.*, 1926, 538). We have been unable to repeat this observation, using pure phenylbenzthiazole, only one tetrabromide (m. p. 134—136°) being isolated. Since benzthiazole prepared by Mohlau's method (*Ber.*, 1888, 21, 59) and not specially purified (p. 131) yields a bromo-addition compound quite distinct from the dibromide and the tetrabromide obtained from the pure base, the original observation was probably due to the presence of an impurity introduced in the thionation process which was used in preparing the original specimen of phenylbenzthiazole from benzylideneaniline.

bond (1 : 2) of benzthiazole would be expected to lead to a decrease in the aromatic characteristics of the heterocyclic nucleus, and the bromination of certain 2-alkyl-1 : 2-dihydrobenzthiazoles was therefore undertaken.

The 1-imino-2-alkyl-1 : 2-dihydrobenzthiazoles (XXI) passed directly into the *hydrotribromides* of the corresponding 5-bromo-derivatives on bromination under the usual conditions. On the other hand, the 1-keto-2-alkyl-1 : 2-dihydrobenzthiazoles (XXII) yielded unstable *tetrabromides*, which were rapidly converted into the corresponding 5-bromo-1-keto-derivatives by loss of bromine and hydrogen bromide.

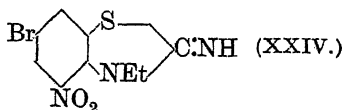
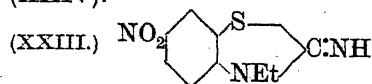
The order of stability of the bromo-addition compounds is therefore the reverse of that observed in the case of the mobile 1-amino- and 1-hydroxy-benzthiazoles.



1-Thio-2-methyl-1 : 2-dihydrobenzthiazole (XX) yielded a *tetra-bromide*, which regenerated the original thioketone on reduction, and could not be converted into a bromo-substitution derivative.

Regarding the Hugershoff reaction, *as*-phenylmethylthiocarbamide gave rise to an unstable *hydropentabromide* of 1-imino-2-methyl-1 : 2-dihydrobenzthiazole, which lost bromine on exposure to air, giving a *hydrodibromide*. The ethyl homologue, however, yielded a stable *hydrotribromide*, which is of interest on account of its behaviour on nitration.

Under conditions of mononitration, the hydrotribromide yielded, approximately in the proportion of 2 : 5, 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole (XXIII) and a bromonitro-derivative, which was also obtained from the mononitration of 5-bromo-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole and its *hydrotribromide* and is presumably 5-bromo-3-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole (XXIV).

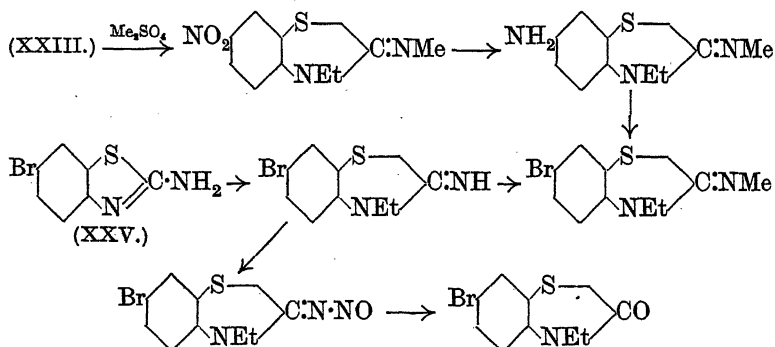


Nitration of the *hydrobromide* of 1-imino-2-ethyl-1 : 2-dihydrobenzthiazole under similar conditions also gave rise to the same products in the approximate proportion of 2 : 1 in favour of the 5-nitro-1-imino-derivative.

The first action of nitric acid (*d* 1.5) is evidently one of decomposition, possibly with the production of nitrosyl bromide, which may act as a brominating agent on the portion of the base initially escaping nitration.

Mononitration of 1-imino-2-ethyl-1:2-dihydrobenzthiazole and its *acetyl* derivative lead to exclusive nitration in the 5-position of the benzthiazole system, and 1-keto-2-ethyl-1:2-dihydrobenzthiazole behaves similarly.

The 5-bromo and 5-nitro-derivatives described in this paper were oriented by means of the following scheme [the constitution of 5-bromo-1-aminobenzthiazole (XXV) follows from its synthesis from *p*-bromophenylthiocarbamide (Hunter, J., 1926, 1397)].



## EXPERIMENTAL.

### *Benzthiazole Derivatives.*

Benzthiazole was prepared by the thionation of dimethylaniline (Mohlau, *Ber.*, 1888, **21**, 59), purified by means of the crystalline nitrate (Mills, J., 1922, **424**, 460), and redistilled over copper turnings. The pure base was a colourless, highly refractive oil, indistinguishable from quinoline in odour, b. p. 227—228°/765 mm.,  $d_{20}^{25}$  1.244. Specimens (b. p. 226—228°) of the base which had not been redistilled over copper, when kept for some months, darkened and acquired the unpleasant odour of the crude thionation product. Such specimens behaved abnormally on bromination (p. 132).

*Benzthiazole Dibromide.*—(i) A solution of the pure base (1.1 c.c.) in chloroform (12 c.c.) was treated at 0—3° with bromine (0.7 c.c. in 2 c.c. of chloroform). After a short time, the *dibromide* crystallised in glistening yellow needles, which were collected on porous earthenware and dried in a vacuum; m. p. 88—90° (decomp.) [Found: N, 4.9; Br (total), 54.5; Br (labile), iodometrically in chloroform containing a few drops of purified acetic acid, 54.4; S, 10.9.  $\text{C}_7\text{H}_5\text{NBr}_2\text{S}$  requires N, 4.7; Br (total and labile), 54.3; S, 10.8%].

(ii) The compound was prepared in a similar manner from benzthiazole (1.2 g.), glacial acetic acid (7 c.c.), and a solution of bromine

(0.7 c.c.) in acetic acid (1 c.c.); m. p. 87—88° (decomp.) [Found: Br (total), 54.1; Br (labile), 54.0%].

The yellow crystals of the dibromide were stable in a vacuum, but rapidly reddened at the edges in moist air. The compound was quantitatively reduced by sulphurous acid, giving a colourless solution from which the original base was recovered by basification and extraction with ether; a similar decomposition, accompanied by evolution of nitrogen, took place when the dibromide was treated with aqueous ammonia (*d* 0.880). It was also decomposed by sulphuric acid at a low temperature (0—3°; 20 c.c. of 99% acid per g. of dibromide) with evolution of hydrogen bromide and regeneration of benzthiazole. *Thermal decomposition.* The dibromide was heated from 60° to 140°/18 mm. in the course of 10 minutes: fusion commenced at 100—105° and was complete at 115°. Reduction of the product by sulphurous acid yielded benzthiazole unaccompanied by the tetrabromo-substitution derivative.

*Benzthiazole Tetrabromide.*—Experiment (i) was repeated, 1.8 c.c. of bromine being used. A *tetrabromide* separated in small scarlet crystals, which were dried on porous earthenware in a vacuum for 5—10 minutes and then analysed; m. p. 67—68° (Found: Br, 70.0.  $C_7H_5NBr_4S$  requires Br, 70.3%). This compound decomposed appreciably on being exposed to the atmosphere for a few minutes; in its reactions, it behaved similarly to the dibromide.\*

When an experiment similar to (i) was performed with benzthiazole which had not been purified by redistillation over copper and had been kept for some months (2 g. of base, 24 c.c. of chloroform, and 1.3 c.c. of bromine), orange crystals of a *bromo-addition* compound separated, which had m. p. 100—103° (decomp.) after drying in a vacuum [Found: Br (total), 63.2; Br (labile), 63.0.  $(C_7H_5NBr_3S)_2$  requires Br, 64.0%]. The substance dissolved in sulphurous acid, yielding a colourless solution from which, on basification and extraction with ether, benzthiazole was obtained; this was identified by its properties and by the analysis of its chloroplatinite (Found: Pt, 28.5. Calc.: Pt, 29.1%).

*3:4:5:6-Tetrabromobenzthiazole.*—When solutions of any of the preceding bromo-addition compounds in 70% alcohol were boiled for a short time and allowed to cool, the *tetrabromobenzthiazole* crystallised in glistening hair-like needles, m. p. 122° (Found: Br, 70.9; S, 6.9.  $C_7HNBr_4S$  requires Br, 70.9; S, 7.1%). This com-

\* Quinoline tetrabromide (Grimaux, *loc. cit.*) was best prepared by treating a solution of quinoline (1 c.c.) in chloroform (12 c.c.) at 25—30° with bromine (2 c.c. in 3 c.c. of chloroform) and shaking the mixture: the temperature rose some 10° and the tetrabromide crystallised in glistening red plates, m. p. 95—97° [Found: Br (total), 70.4; Br (labile), 69.2. Calc.: Br, 71.3%].



pound was recovered unchanged after being heated under reflux in alcoholic solution containing about 10% of hydrochloric acid for 40 hours; and also after being heated (0.5 g.) with tin (1 g.) and concentrated hydrochloric acid (20 c.c.) for  $\frac{1}{2}$  hour. An attempt to reduce it (0.5 g.) in absolute alcohol (20 c.c.) with sodium (0.4 g.) also proved unsuccessful. The tetrabromobenzthiazole has no basic properties in the ordinary sense; although it dissolves in 98–99% sulphuric acid, it is reprecipitated by dilution with water. All attempts to prepare a bromo-addition compound of the tetrabromobenzthiazole proved unsuccessful.

*1-Aminobenzthiazole Dibromide*.—When a solution of 1.5 g. of 1-aminobenzthiazole in 50 c.c. of chloroform at 0° was gradually treated with a solution of bromine (0.7 c.c.) in the same solvent (3 c.c.), a yellow precipitate was produced which redissolved, giving a clear solution; the *dibromide* then separated in small, soft, orange-pink crystals, which were rapidly dried in a vacuum. This compound became pale yellow at 160–170° and had m. p. 265° (decomp.) (Found: Br, 51.8.  $C_7H_6N_2Br_2S$  requires Br, 51.5%).

A solution of the compound in purified acetic acid liberated iodine from potassium iodide, but the iodometric titre was always low (ca. 30%) on account of partial isomerisation into the hydrobromide of 5-bromo-1-aminobenzthiazole.

The dibromide was converted into 5-bromo-1-aminobenzthiazole hydrobromide by exposure to air; the change, which was accompanied by loss of colour, was appreciable in  $\frac{1}{4}$  hour and complete in less than 20 hours. The product was identified by its m. p. (265°), by the m. p. of the base liberated by alkali (210°), and by the m. p. of the acetyl derivative of the latter (222°). The dibromide was also isomerised by cold acetic anhydride.

*1-Aminobenzthiazole tetrabromide*, obtained by employing an excess of bromine, formed small, soft, dark reddish-brown plates, m. p. 266° (decomp.; sintering with loss of bromine at 170°) (Found: Br, 67.6.  $C_7H_6N_2Br_4S$  requires Br, 68.1%).

*1-Aminobenzthiazole Hydrodibromide (Hugershoff's Dibromide)*.—(i) A suspension of 1.5 g. of finely ground phenylthiocarbamide in 15 c.c. of chloroform was rapidly treated with bromine (1.4 c.c. in 1.4 c.c. of chloroform), and the mixture heated under reflux for 2–3 minutes. The *hydrodibromide* separated from the hot solution in glistening, orange-coloured, rhombic crystals, which were crushed on porous earthenware and dried in a vacuum; m. p. 127–128° (decomp. with efferv. at 131°) [Found: Br (total), 51.4; Br (labile), 24.9; S, 10.3.  $C_7H_6N_2S \cdot HBr(Br)$  requires Br (total), 51.5; Br (labile), 25.6; S, 10.3%].

(ii) Bromine (1.6 c.c.) was added to a boiling solution of 1-amino-

benzthiazole (1 g.) in glacial acetic acid (24 c.c.) containing 4 g. of hydrogen bromide. The hydrodibromide crystallised in large orange-red prisms, m. p. 128—130° after drying in a vacuum [Found: Br (total), 51.2; Br (labile), 24.6; S, 10.6%]. A mixture of the two specimens melted at 128—130°.

This compound remained unchanged in a vacuum, or over potassium hydroxide in a desiccator. On prolonged exposure to the atmosphere (8—9 months), it lost bromine, yielding 1-aminobenzthiazole hydrobromide, m. p. 231—232°.

When the compound (3 g.) was heated with acetic anhydride (7 c.c.), the solution developed a pink colour and a white precipitate (2.2 g.) separated, containing impure 5-bromo-1-acetamidobenzthiazole (0.25 g.), which was identified by mixed m. p. and by hydrolysis to 5-bromo-1-aminobenzthiazole by 60% sulphuric acid, and 1-aminobenzthiazole hydrobromide (1.8 g.).

*Thermal decomposition.* A flask containing the hydrodibromide (1.7 g.) was exhausted to 11 mm., placed in an oil-bath at 125°, and heated to 210° in the course of  $\frac{1}{4}$  hour; decomposition was then complete. The greyish-white granular residue (1.25 g.) consisted of 1-aminobenzthiazole hydrobromide, m. p. 228°. *Dissociation experiments.* (i) Three experiments were made with specimens of the hydrodibromide of different surface areas: the specimens were heated at 90—100°/10 mm. for 10 minutes, and the residues analysed for labile bromine. The results [Found: Br (labile), 20.8, 19.6, 19.9%] indicate that this factor has only a slight effect on the dissociation. (ii) Two similar experiments were performed at 97—98°/12 mm. for 2 minutes [Found: Br (labile), 24.1, 23.8%]. The degree of dissociation in these circumstances is about 5%.

*1-Anilino benzthiazole Tetrabromide.*—Hugershoff's tetrabromide (Ber., 1903, 36, 3121) crystallised in red needles, m. p. 127° (decomp.) (previously given, J., 1925, 127, 2025, as 117°) [Found: Br (total), 58.8; Br (labile), 40.1. Calc. for  $C_{13}H_{10}N_2S_2HBr(Br_3)$ : Br (total), 58.6; Br (labile), 43.9%]. The *hydrotribromide* had m. p. 130° (decomp.) (previously given as 125°) [Found: Br (total), 51.5; Br (labile), 32.5. Calc. for  $C_{13}H_{10}N_2S_2HBr(Br_2)$ : Br (total), 51.7; Br (labile), 34.4%]. The *hydrotetrabromide* was also prepared from a solution of the anilino-base (0.5 g.) and hydrogen bromide (0.5 g.) in glacial acetic acid (5.5 c.c.) and bromine (0.5 c.c.), and identified by m. p., mixed m. p., and analysis [Found: Br (total), 58.4; Br (labile), 39.8%].

*1-p-Toluidino-5-methylbenzthiazole hydrotetrabromide*, prepared from *s-di-p-tolylthiocarbamide* (J., 1925, 127, 2027), formed red needles, m. p. 130—132° (decomp.) (previously given as 145°) [Found:

Br (total), 55.2; Br (labile), 36.6. Calc. for  $C_{15}H_{14}N_2S, HBr(Br_3)$ : Br (total), 55.6; Br (labile), 41.7%. Its composition was not appreciably affected by keeping over potassium hydroxide in a desiccator for 2 days [Found: Br (labile), 36.4%]. It was also prepared from the toluidinobenzthiazole and hydrogen bromide in acetic acid and excess of bromine, and identified by m. p., mixed m. p., and analysis [Found: Br (labile), 36.4%]. The *hydrotribromide* had m. p. 145–147° (previously given as 148°) [Found: Br (total), 48.8; Br (labile), 31.5. Calc. for  $C_{15}H_{14}N_2S, HBr(Br_2)$ : Br (total), 48.5; Br (labile), 32.3%]. 3:2'-Dibromo-1-anilino-5:4'-dimethylbenzthiazole, prepared by heating a mixture of *s*-di-*o*-bromo-*p*-tolylthiocarbamide (0.5 g.), chloroform (6 c.c.), and bromine (0.6 c.c.) under reflux for 15 minutes and reducing the product with sulphurous acid, separated from alcohol in small prisms, m. p. 159–160°, which did not depress the m. p. of a specimen of the dibromotoluidinobenzthiazole described in 1925 (J., 127, 2027).

5:4'-Dibromo-1-anilino-3:2'-dimethylbenzthiazole.—(i) The dibromo-base obtained from the hydrohexabromide of 1-*o*-toluidino-3-methylbenzthiazole (J., 1925, 127, 2026) separated from alcohol-ethyl acetate in small needles, m. p. 210–211° (Found: Br, 38.6. Calc.: Br, 38.9%).

(ii) The *bromo*-addition compound obtained by heating a mixture of *s*-di-*p*-bromo-*o*-tolylthiocarbamide (1 g.), chloroform (17 c.c.), and bromine (1.3 c.c.) under reflux for 15 minutes formed dark crimson crystals, which became colourless at 180–190° and charred at 270° (Found: Br, 60.0.  $C_{15}H_{12}N_2Br_2S, HBr(Br_2)$  requires Br, 61.3%). 5:4'-Dibromo-1-anilino-3:2'-dimethylbenzthiazole obtained by reduction of this bromo-addition compound proved identical with that described under (i).

*The Mobility of 1-Hydroxybenzthiazole. Synthesis from 1-Chlorobenzthiazole and from o-Aminophenylmercaptan and Carbonyl Chloride.*

—(i) 1-Hydroxybenzthiazole was prepared by heating an alcoholic solution of 1-chlorobenzthiazole containing hydrochloric acid for 25 hours; on recrystallisation from alcohol, it formed glistening prisms, m. p. 138°.

(ii) *Claasz's experiment.* 25 G. of a 12% solution of carbonyl chloride in toluene were added to an ethereal solution of *o*-aminophenylmercaptan (2.5 g. in 40 c.c.) and the mixed liquids were decanted from the precipitate of *o*-aminophenylmercaptan hydrochloride and evaporated on a steam-bath. Extraction of the resulting oil with alkali, acidification of the extract, extraction with chloroform, and recrystallisation of the product from methyl alcohol yielded 1-hydroxybenzthiazole, which melted at 128–130° and at 134° when mixed with a genuine specimen prepared by Hofmann's

method. The identity was confirmed by conversion of the product into 5-bromo-1-hydroxybenzthiazole, identical with that prepared by other methods.

(iii) A solution of *o*-aminophenylmercaptan (1.2 c.c.) in chloroform (10 c.c.) was treated with carbonyl chloride from a cylinder for  $\frac{1}{2}$  hour, the mixture evaporated on a steam-bath, and the product extracted with ether. After removal of the ether, the crystalline residue separated from methyl alcohol in prisms (0.9 g.), m. p.  $135^{\circ}$ , and  $135\text{--}136^{\circ}$  when mixed with the specimen prepared under (i).

*Methylation of 1-Hydroxybenzthiazole and the Isolation of 1-Keto-2-methyl-1:2-dihydrobenzthiazole.*—1-Hydroxybenzthiazole was recovered unchanged after it had been heated with methyl sulphate (1.5 c.c. for 1 g.) at  $100^{\circ}$  for  $\frac{1}{2}$  hour, the solution diluted with water (8 c.c.), and the heating continued for another hour.

4 C.c. of methyl sulphate were added to a mixture of 0.5 g. of 1-hydroxybenzthiazole and 1 c.c. of chloroform in 10 c.c. of 25% potassium hydroxide solution and the whole was shaken and kept for an hour. Extraction with chloroform and slow removal of the solvent yielded a gum which set to a crystalline mass of 1-keto-2-methyl-1:2-dihydrobenzthiazole, m. p.  $74^{\circ}$ , and  $76^{\circ}$  when mixed with an authentic specimen prepared from the 1-nitrosoimino-derivative (Besthorn, *Ber.*, 1910, 43, 1523). The identity was further established by conversion of the product into 5-bromo-1-keto-2-methyl-1:2-dihydrobenzthiazole, which melted at  $126\text{--}127^{\circ}$  alone and when mixed with the specimen described on p. 140.

*Bromination of 1-Hydroxybenzthiazole and the Synthesis of 5-Bromo-1-hydroxybenzthiazole from 1-Chloro-5-bromobenzthiazole and from p-Bromophenylthiourethane by Way of 5-Bromo-1-ethoxybenzthiazole.*—(i) When a solution of 0.5 g. of 1-hydroxybenzthiazole in chloroform (6 c.c.) was treated with 0.5 c.c. of bromine at  $0\text{--}3^{\circ}$ , hydrogen bromide was evolved; the solution was concentrated under reduced pressure at laboratory temperature, and 5-bromo-1-hydroxybenzthiazole obtained. On recrystallisation from methyl alcohol, this formed needles, m. p.  $225\text{--}226^{\circ}$  (Found: Br, 35.1.  $\text{C}_7\text{H}_4\text{ONBrS}$  requires Br, 34.8%). It dissolved in alkalis and was reprecipitated by mineral acids. It was recovered unchanged after being heated with methyl iodide (more than 3 equivs.) at  $100^{\circ}$  for 25 hours.

(ii) 0.5 G. of 1-chloro-5-bromobenzthiazole (b. p.  $158\text{--}159^{\circ}/18$  mm.; Dyson, Hunter, and Soyka, *J.*, 1929, 461) was heated with alcohol, containing hydrochloric acid, for 40–45 hours. The resulting solution was made alkaline, filtered, and acidified with 20% acetic acid. The precipitate of 5-bromo-1-hydroxybenzthiazole was recrystallised from alcohol and identified by m. p. and mixed m. p. determination with the specimen prepared in (i).

(iii) *p*-Bromophenylthiourethane, prepared in 80–90% yield by heating a solution of *p*-bromophenylthiocarbimide (15 g.) in absolute alcohol (100 c.c.) under reflux for 30 hours, separated from methyl alcohol in prisms, m. p. 106–107° (Found: S, 12.5.  $C_9H_{10}ONBrS$  requires S, 12.3%).

5-Bromo-1-ethoxybenzthiazole. 10 G. of *p*-bromophenylthiourethane, previously ground with a little alcohol, were dissolved in 75 c.c. of 30% aqueous sodium hydroxide; the solution was diluted to 200 c.c. with water and added in 20 c.c. portions at 5-minute intervals to a well-stirred solution of potassium ferricyanide (60 g.) in water (300 c.c.) which was maintained at 80–90°. Extraction with ether yielded a brown oil, which was distilled in steam; the bromoethoxybenzthiazole obtained (yield, 35%) separated from 90% methyl alcohol in pale yellow plates, m. p. 75–76° (Found: Br, 31.4.  $C_9H_8ONBrS$  requires Br, 31.0%). *Hydrolysis*. A solution of the bromoethoxythiazole in 40% hydrobromic acid was heated under reflux for 20 minutes and cooled; crystals then separated. The mixture was diluted with water and extracted with chloroform and the chloroform was removed on a steam-bath; the 5-bromo-1-hydroxybenzthiazole obtained crystallised from methyl alcohol in needles, m. p. 222–223°, 223° when mixed with the specimen prepared in (i).

*The Mobility of 1-Thiolbenzthiazole. Synthesis by Hofmann's Method and from o-Aminophenylmercaptan and Thiocarbonyl Chloride*.—(i) 1-Thiolbenzthiazole was prepared by heating a solution of *o*-aminophenylmercaptan (3 g.) in alcohol (10 c.c.) and carbon disulphide (15 c.c.) under reflux for 8 hours. After two recrystallisations from methyl alcohol (animal charcoal), it formed colourless needles, m. p. 179° (Hofmann, *Ber.*, 1887, 20, 1879; Jacobson and Frankenbacher, *Ber.*, 1891, 24, 1403, recorded m. p. 174°).

(ii) Thiocarbonyl chloride (1 c.c.) in chloroform (2 c.c.) was gradually added to *o*-aminophenylmercaptan (2 c.c.) in chloroform (10 c.c.) at 5°, the mixture being shaken after each addition. A vigorous reaction took place with the separation of yellow crystals; the chloroform and the excess of thiocarbonyl chloride were removed on a steam-bath, the product was extracted with ether (8 extractions), and the united extracts were filtered from the hydrochloride of *o*-aminophenylmercaptan. On removal of the ether and subsequent recrystallisation from methyl alcohol, 1-thiolbenzthiazole (0.7 g.) was obtained in pale yellow needles, m. p. 176–177°, and 177–179° when mixed with the specimen prepared by Hofmann's method.

*Methylation*. A mixture of 1-thiolbenzthiazole (1 g.), methyl sulphate (3 c.c.), and methyl alcohol (3 c.c.) was heated under reflux

for an hour. The solution was cooled, the excess of methyl sulphate decomposed with aqueous ammonia ( $d$  0.880), and the mixture extracted while still warm with chloroform. A clear gum was obtained which on crystallisation from methyl alcohol yielded 0.9—1 g. of 1-methylthiolbenzthiazole in colourless prisms, *m. p.* 47—49°.

*Bromination of 1-Thiolbenzthiazole.*—A solution of the thiol (1 g.) in chloroform (50 c.c.) was treated with bromine (1.5 c.c. in an equal volume of the same solvent) at 10°; the *tetrabromide* formed orange plates, *m. p.* 147° (decomp. with efferv. after previous shrinking) (Found: Br, 65.6.  $C_7H_5NBr_4S_2$  requires Br, 65.7%). On reduction with sulphurous acid, the tetrabromide yielded benzthiazolyl 1 : 1-disulphide, which crystallised from acetic acid in silvery plates, *m. p.* 180°, and 180—181° when mixed with a genuine specimen. (A mixture of this product with 1-thiolbenzthiazole melted at about 140°.)

*1-Phenylbenzthiazole Tetrabromide.*—1 G. of the base, purified by distillation under reduced pressure, was brominated as previously described (Hunter, J., 1926, 539); the *tetrabromide* crystallised in orange-red plates, *m. p.* 134—136° [Found: Br (total), 60.0; Br (labile), 45.3. Calc. for  $C_{13}H_9NBr_4S$ : Br, 60.25%]. Further crops of crystals, *m. p.* 130—132°, of the same tetrabromide were obtained from the mother-liquor by concentration under reduced pressure at laboratory temperature [Found: Br (labile), 45.0%].

*Action of mercuric oxide.* (i) When a mixture of precipitated mercuric oxide (1 g.) and the tetrabromide (0.6 g.) in chloroform (50 c.c.) was shaken, the colour was discharged. Evaporation of the filtered solution on a steam-bath yielded 1-phenylbenzthiazole unaccompanied by any trace of the 5-bromo-derivative (Bogert and Abrahamson, *J. Amer. Chem. Soc.*, 1922, 44, 826).

(ii) A similar result was obtained with "dry" materials, excepting that the discharge of colour was somewhat retarded.

By treating a solution of 1-phenylbenzthiazole (1 g.) in chloroform (11 c.c.) with bromine (1.4 c.c.) at 0°, a red oil was obtained which sometimes crystallised in red needles; the *hexabromide* was unstable, *m. p.* 156° (decomp. with efferv. after sintering with loss of bromine over a range of about 40°) (Found: Br, 67.2.  $C_{13}H_9NBr_6S$  requires Br, 69.5%).

#### *Benzoxazole and Benzselenazole Derivatives.*

*Bromination of 1-Phenylbenzoxazole.*—A solution of the phenylbenzoxazole (Ladenburg, *Ber.*, 1876, 9, 1524) (0.5 g.) in chloroform (4 c.c.) was treated with bromine (0.9 c.c. in 1 c.c. of chloroform) at 0°. After an hour, the *hexabromo*-addition compound separated in small, soft, red crystals, *m. p.* 153—155° after rapid drying on

porous earthenware in a vacuum [Found: Br (total), 73.8; Br (labile), 54.9.  $C_{13}H_9ONBr_6$  requires Br, 71.1%]. This substance lost bromine when kept over potassium hydroxide in a vacuum for 2 hours, giving a stable, yellow, microcrystalline *hydrotribromide* of 5(?)-bromo-1-phenylbenzoxazole, m. p. 154—155° (with previous shrinking) [Found: Br (total), 61.8; Br (labile), 31.5.  $C_{13}H_8ONBr, HBr(Br_2)$  requires Br (total), 62.1; Br (labile), 31.1%]. A specimen of this compound prepared from the bromo-substituted benzoxazole, hydrogen bromide, and bromine in acetic acid had a higher m. p. (164—166° after previous shrinking) [Found: Br (labile), 31.3%], but lacked the stability in moist air of the specimen obtained from the hexabromide.

5(?) - *Bromo-1-phenylbenzoxazole*, obtained by reduction of the hydrotribromide with sulphurous acid, or by dissolution of the hexabromide in alcohol, crystallised from methyl alcohol in small needles, m. p. 106—107° (Found: Br, 28.3.  $C_{13}H_8ONBr$  requires Br, 29.1%).

1-*Phenylbenzselenazole tetrabromide*, obtained from the selenazole, chloroform, and excess of bromine at 0°, and also at 18°, crystallised in orange-red needles, m. p. 148° [Found: Br (total), 55.1; Br (labile), 41.0.  $C_{13}H_9NBr_4Se$  requires Br, 55.4%]. It regenerated the original phenylselenazole on treatment with sulphurous acid, but all attempts to prepare a 5-bromo-substitution derivative led only to brown gummy products, which could not be crystallised.

### 1 : 2-Dihydrobenzthiazole Derivatives.

1-*Imino-2-methyl-1 : 2-dihydrobenzthiazole Hydropentabromide*.—A solution of *as*-phenylmethylthiocarbamide (1 g.) in chloroform (10 c.c.) was treated with bromine (2 c.c. in 3 c.c. of the same solvent) and heated under reflux for a few minutes. The *hydropentabromide* crystallised in red plates (or needles), m. p. 121—122° (decomp. with efferv.), which were rapidly dried in a vacuum and immediately analysed [Found: N, 5.25; Br (total), 71.0; Br (labile), 57.0; S, 5.7.  $C_8H_8N_2S, HBr(Br_4)$  requires N, 4.95; Br (total), 70.8; Br (labile), 56.7; S, 5.6%]. On exposure to air for some weeks, it lost bromine, giving a stable, yellow, insoluble *hydrodibromide*, m. p. 194—196° (decomp.; sintering at 190°) [Found: Br, 49.3.  $C_8H_8N_2S, HBr(Br)$  requires Br, 49.4%]. Both compounds yielded 1-imino-2-methyl-1 : 2-dihydrobenzthiazole, m. p. 123°, on reduction with sulphurous acid, but failed to undergo nuclear substitution when heated with alcohol, giving the *hydrobromide* of 1-imino-2-methyl-1 : 2-dihydrobenzthiazole (prepared also from the base and hydrogen bromide) in small needles, m. p. 275° (decomp.) (Found: Br, 32.5.  $C_8H_8N_2S, HBr$  requires Br, 32.8%). The hydropenta-

bromide was also prepared by treating a solution of the hydrobromide in glacial acetic acid with excess of bromine.

*1-Acetimido-2-methyl-1:2-dihydrobenzthiazole*, prepared by acetylation of the imino-base with acetic anhydride, crystallised from alcohol in needles, m. p. 141—142° (Found: S, 15.8.  $C_{10}H_{10}ON_2S$  requires S, 15.5%).

*Bromination of 1-Imino-2-methyl-1:2-dihydrobenzthiazole*.—The *hydrotribromide* of 5-bromo-1-imino-2-methyl-1:2-dihydrobenzthiazole, obtained by treatment of the imino-base (0.5 g.) in chloroform (15 c.c.) with bromine (1 c.c. in 2 c.c. of the same solvent) at 0°, formed orange-yellow crystals which lost bromine at 100—110° and were unmelted at 280° [Found: N, 5.8; Br (total), 66.2; Br (labile), in acetic acid, 33.4; S, 6.6.  $C_8H_7N_2BrS \cdot HBr(Br_2)$  requires N, 5.8; Br (total), 66.1; Br (labile), 33.0; S, 6.6%]. The *hydrobromide* of 5-bromo-1-imino-2-methyl-1:2-dihydrobenzthiazole, obtained by boiling a solution of the hydrotribromide in alcohol, formed small needles, which were unmelted at 290° [Found: Br, 49.3.  $C_8H_7N_2BrS \cdot HBr$  requires Br, 49.3%]. The *5-bromo-base* crystallised with difficulty from methyl alcohol in needles, m. p. 110° (Found: N, 11.8; Br, 32.9; S, 13.4.  $C_8H_7N_2BrS$  requires N, 11.5; Br, 32.7; S, 13.2%). The *acetyl* derivative, prepared by means of acetic anhydride, crystallised from much ethyl acetate in feathery needles, m. p. 219—220° (Found: N, 9.8; Br, 28.2.  $C_{10}H_9ON_2BrS$  requires N, 9.8; Br, 28.05%).

*Bromination of 1-Keto-2-methyl-1:2-dihydrobenzthiazole and the Synthesis of 5-Bromo-1-keto-2-methyl-1:2-dihydrobenzthiazole from 5-Bromo-1-imino-2-methyl-1:2-dihydrobenzthiazole by Way of 5-Bromo-1-nitrosoimino-2-methyl-1:2-dihydrobenzthiazole*.—When a solution of 1-keto-2-methyl-1:2-dihydrobenzthiazole (0.4 g.) in chloroform (4 c.c.) was treated with bromine (0.5 c.c. in 1 c.c. of chloroform) at 0°, traces of hydrogen bromide were evolved and a dark purple-brown *tetrabromide* separated, which was rapidly dried in a vacuum and immediately analysed (Found: Br, 67.8.  $C_8H_7ONBr_4S$  requires Br, 65.9%). It softened at 100° and melted to a clear red liquid at 120°; in a vacuum, it lost bromine, yielding red crystals, m. p. 101—103°, of a substance having the composition of a *dibromide* (Found: Br, 48.6.  $C_8H_7ONBr_2S$  requires Br, 49.2%). *5-Bromo-1-keto-2-methyl-1:2-dihydrobenzthiazole* crystallised in feathery tufts of silky needles, m. p. 126—127° (Found: N, 5.9; Br, 32.5; S, 13.2.  $C_8H_6ONBrS$  requires N, 5.7; Br, 32.6; S, 13.1%).

*5-Bromo-1-nitrosoimino-2-methyl-1:2-dihydrobenzthiazole*.—A solution of 5-bromo-1-imino-2-methyl-1:2-dihydrobenzthiazole (2 g.) in glacial acetic acid (16 c.c.) was kept at 15° during the addition



of a solution of sodium nitrite (1 g.) in water (5 c.c.), the mixture being well shaken; the *nitroso*-derivative soon separated in orange crystals (2.1 g.), which exploded at  $161^{\circ}$  (Found: N, 15.5.  $C_8H_6ON_3BrS$  requires N, 15.4%).

A solution of the nitroso-compound (1 g.) in xylene (6 c.c.), when heated, turned yellow and nitrogen was evolved; the solution was concentrated to about 2 c.c., diluted with methyl alcohol, boiled with animal charcoal, filtered, and concentrated; 5-bromo-1-keto-2-methyl-1:2-dihydrobenzthiazole (0.8 g.) was obtained in slender needles, m. p.  $126-127^{\circ}$ , alone and when mixed with the specimen already described.

1-Thiol-2-methyl-1:2-dihydrobenzthiazole tetrabromide, prepared from the thiol derivative and bromine in chloroform, formed small orange crystals, m. p.  $124-126^{\circ}$  (decomp.; reddening at  $115-120^{\circ}$ ) (Found: Br, 63.7; S, 12.6.  $C_8H_7NBr_4S_2$  requires Br, 63.9; S, 12.8%). When heated with absolute alcohol, it rapidly regenerated the original thiol derivative.

The bromination of 1-nitrosoimino-2-methyl-1:2-dihydrobenzthiazole yielded a brown tetrabromide, m. p.  $280^{\circ}$  (decomp.) (Found: Br, 61.9.  $C_8H_7ON_3Br_4S$  requires Br, 62.4%).

1-Imino-2-ethyl-1:2-dihydrobenzthiazole is conveniently prepared in quantity by the following method, which is generally applicable to iminoalkyldihydrobenzthiazoles and alkylaminobenzthiazoles. A solution of *as*-phenylethylthiocarbamide (50 g.) in chloroform (250 c.c.) was treated with bromine (30 c.c. in 50 c.c. of the same solvent) with cooling. After being heated under reflux for 10 minutes, the mixture was treated with excess of sulphurous acid and basified, and the product obtained by removal of the chloroform was recrystallised from alcohol, the iminoethyldihydro-derivative forming large crystals, m. p.  $84-85^{\circ}$ . Yield, 49 g. (98%).

1-Imino-2-ethyl-1:2-dihydrobenzthiazole hydrotribromide, prepared from 1.5 g. of the ethylthiocarbamide in chloroform (12 c.c.) and bromine (2 c.c.), crystallised from the hot solution in orange-red plates, m. p.  $160-161^{\circ}$  (decomp.) [Found: N, 6.9; Br (total), 57.5; Br (labile), 38.5.  $C_9H_{10}N_2S_3HBr(Br_2)$  requires N, 6.7; Br (total), 57.3; Br (labile), 38.2%]. It was also prepared from the imino-base (0.5 g.) and hydrogen bromide (1 g.) in glacial acetic acid (9 c.c.) and bromine (1 c.c.). The alleged tetrabromide previously described (J., 1926, 1394) was a "wet" specimen of the hydrotribromide. An alcoholic solution of this compound, on being concentrated, yielded the *hydrobromide* of 1-imino-2-ethyl-1:2-dihydrobenzthiazole (which was also prepared from the base and hydrobromic acid) in plates, m. p.  $247-248^{\circ}$  (decomp.) (Found:

Br, 30.5.  $C_9H_{10}N_2S.HBr$  requires Br, 30.9%). 1-Acetimido-2-ethyl-1:2-dihydrobenzthiazole formed prisms, m. p. 127—128° (Found: N, 13.0; S, 14.6.  $C_{11}H_{12}ON_2S$  requires N, 12.7; S, 14.55%).

*Bromination of 1-Imino-2-ethyl-1:2-dihydrobenzthiazole and the Ethylation of 5-Bromo-1-aminobenzthiazole.*—(i) The hydrotribromide of 5-bromo-1-imino-2-ethyl-1:2-dihydrobenzthiazole, obtained by bromination of the imino-base, crystallised in orange needles, m. p. 182—184° (decomp.) [Found: Br (total), 64.2; Br (labile), iodometrically in acetic acid, 32.6.  $C_9H_9N_2BrS.HBr(Br_2)$  requires Br (total), 64.2; Br (labile), 32.1%]. It was also prepared from the 5-bromo-base, hydrogen bromide, and bromine in acetic acid. Attempts to isolate an intermediate bromo-addition compound of the iminoethyl base by using dried materials were unsuccessful. The hydrotribromide was completely dissociated into the hydrobromide and bromine on being heated from 150° to 220°/16 mm. in the course of  $\frac{1}{2}$  hour. 5-Bromo-1-imino-2-ethyl-1:2-dihydrobenzthiazole formed a tenacious gum, which crystallised with difficulty from 80% methyl alcohol in small needles, m. p. 68—70° (Found: Br, 30.7.  $C_9H_9N_2BrS$  requires Br, 31.1%). The acetyl derivative formed silvery needles, m. p. 187° (Found: Br, 26.7; S, 10.7.  $C_{11}H_{11}ON_2BrS$  requires Br, 26.7; S, 10.7%). The hydrobromide crystallised from alcohol, containing a small quantity of hydrogen bromide, in small needles, m. p. 270—272° (Found: Br, 47.0.  $C_9H_9N_2BrS.HBr$  requires Br, 47.3%).

(ii) A mixture of 5-bromo-1-aminobenzthiazole (0.5 g.) and ethyl iodide (1.5 c.c.) was heated at 100° for 18 hours, and the product basified and extracted with chloroform. After removal of the chloroform a gum remained which could not be crystallised. On acetylation, 5-bromo-1-acetimido-2-ethyl-1:2-dihydrobenzthiazole was obtained unaccompanied by other products; it was identified by m. p. and mixed m. p. determination. No trace of the isomeric 5-bromo-1-ethylaminobenzthiazole, m. p. 158° (previously misrecorded by Hunter and Soyka, J., 1926, 2962, as 256°), could be detected.

*Nitration of 1-Imino-2-ethyl-1:2-dihydrobenzthiazole and the Orientation of 5-Nitro-1-imino-2-ethyl-1:2-dihydrobenzthiazole.*—(i) 10 G. of the imino-base were added to 50 c.c. of nitric acid ( $d$  1.5) at 8° in the course of 40 minutes, the temperature not being allowed to rise above 10°. The solution was poured into 400 c.c. of water, the precipitated nitrate [small orange-pink crystals, m. p. 210—212° (decomp.), from alcohol] decomposed with 25% aqueous sodium hydroxide, and the nitro-base recrystallised from alcohol (yield, 9 g.). A further quantity (0.5—1 g.) was obtained by

basifying the filtrate from the nitrate and extracting it with chloroform. 5-Nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole forms small orange-yellow needles, m. p. 139—140° (Found : N, 19.3; S, 14.4.  $C_9H_9O_2N_3S$  requires N, 18.9; S, 14.4%). The acetyl derivative crystallised from much ethyl acetate in soft, pale yellow needles, m. p. 242—243° (Found : N, 16.2; S, 12.2.  $C_{11}H_{11}O_3N_3S$  requires N, 16.0; S, 12.1%).

(ii) *Methylation of 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole.* 6 C.c. of methyl sulphate were added to a suspension of 5 g. of the 5-nitro-1-imino-base in water (100 c.c.) and the mixture was boiled for 40 minutes and then basified with warm 20% sodium hydroxide solution. On recrystallisation from alcohol and thereafter from methyl alcohol, 1 g. of 5-nitro-1-methylimino-2-ethyl-1 : 2-dihydrobenzthiazole was obtained (m. p. 140°, depressed to 115—118° by admixture with 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole), which yielded the pure compound (see below) on further recrystallisation.

(iii) *Methylation of 1-imino-2-ethyl-1 : 2-dihydrobenzthiazole and nitration of 1-methylimino-2-ethyl-1 : 2-dihydrobenzthiazole.* A mixture of 20 g. of 1-imino-2-ethyl-1 : 2-dihydrobenzthiazole, 100 c.c. of water, and 22 c.c. of methyl sulphate was boiled under reflux for 1½ hours. The product was made strongly alkaline with potassium hydroxide, boiled, and extracted with chloroform, and the chloroform removed through a fractionating column. The residual 1-methylimino-2-ethyl-1 : 2-dihydrobenzthiazole, a viscous oil which could not be crystallised, was added drop by drop with continuous shaking to 100 c.c. of nitric acid ( $d$  1.5) at  $-2^\circ$  in the course of an hour, the temperature not being allowed to rise above  $7^\circ$ . The nitration mixture was poured into water (1000 c.c.) and basified; the nitro-base (23—24 g.), recrystallised from alcohol-ethyl acetate and thereafter from methyl alcohol (animal charcoal), formed yellow plates (10 g.), m. p. 154° (Found : N, 18.0; S, 13.6.  $C_{10}H_{11}O_2N_3S$  requires N, 17.7; S, 13.5%).

(iv) *5-Amino-1-methylimino-2-ethyl-1 : 2-dihydrobenzthiazole.* The 5-nitro-compound (7 g.) was heated with tin (14 g.) and concentrated hydrochloric acid (100 c.c.) on a steam-bath for 20 minutes, and the mixture was diluted with 150 c.c. of water, filtered, and made strongly alkaline with 30% potassium hydroxide solution. The 5-amino-base, which was isolated by extraction with chloroform, crystallised from methyl alcohol in small plates (3.5—4 g.), m. p. 124—125° (Found : S, 15.2.  $C_9H_{11}N_3S$  requires S, 15.5%). It dissolved in concentrated hydrochloric acid, giving a pink solution which became pale yellow and finally colourless on dilution with water; on diazotisation, it yielded a diazonium chloride which

coupled with alkaline  $\beta$ -naphthol, giving a red azo-dye. The amino-base slowly darkened and after some weeks the m. p. was  $115^{\circ}$ .

(v) *5-Bromo-1-methylimino-2-ethyl-1:2-dihydrobenzthiazole*. (A) A diazotised solution of the 5-amino-base (2.4 g.) in 20% hydrochloric acid (9 c.c.) was added to a cuprous bromide solution (prepared from 4.5 g. of copper sulphate crystals) at  $0^{\circ}$ . The mixture was heated on a steam-bath for  $\frac{1}{4}$  hour and basified; the black oil obtained, isolated by means of chloroform, yielded yellowish needles of *5-bromo-1-methylimino-2-ethyl-1:2-dihydrobenzthiazole*, m. p.  $89^{\circ}$ , on crystallisation from methyl alcohol (animal charcoal) (Found: Br, 29.05.  $C_{10}H_{11}N_2BrS$  requires Br, 29.1%). Yield, 60–70%. (B) A cleaner product was obtained by Gattermann's method. 0.8 G. of the amino-base was dissolved in 6 c.c. of hydrobromic acid ( $d$  1.45) and water (3 c.c.) and diazotised; finely divided copper (prepared from 0.6 g. of zinc dust and 1.8 g. of copper sulphate crystals) having been added, the mixture was heated on a steam-bath for 10 minutes, diluted with 20 c.c. of water, basified, and extracted with chloroform. The 5-bromo-base obtained on recrystallisation from methyl alcohol was identical with that prepared in (A) and (C). (C) A mixture of 5-bromo-1-imino-2-ethyl-1:2-dihydrobenzthiazole (1 g.), water (10 c.c.), and methyl sulphate (1.5 c.c.) was heated under reflux for  $\frac{1}{2}$  hour, boiled with excess of 30% alkali solution, and extracted with chloroform. The oil obtained from the extract was dissolved in absolute methyl alcohol; when the solution was concentrated under reduced pressure at laboratory temperature, the methyl derivative sometimes crystallised in colourless needles which alone and when mixed with the specimens synthesised from 5-amino-1-methylimino-2-ethyl-1:2-dihydrobenzthiazole, melted at  $88$ – $89^{\circ}$  (Found: Br, 29.1%).

*Dinitration of 1-Imino-2-ethyl-1:2-dihydrobenzthiazole*.—(i) The iminoethyl base (2 g.) was gradually added to 20 c.c. of nitric acid ( $d$  1.5), the temperature rising to  $55^{\circ}$ . The mixture was poured into 100 c.c. of water; the precipitated nitrate, decomposed with 20% potassium hydroxide solution, gave *dinitroiminoethyl-dihydrobenzthiazole*, which crystallised from methyl alcohol-ethyl acetate in golden plates, m. p.  $242$ – $244^{\circ}$  (Found: N, 21.2.  $C_9H_8O_4N_4S$  requires N, 20.9%). The alkaline liquid on acidification yielded a substance which separated from methyl alcohol-ethyl acetate in yellow-brown needles, m. p.  $200^{\circ}$ .

(ii) *5-Nitro-1-imino-2-ethyl-1:2-dihydrobenzthiazole* (0.5 g.) was gradually added to 10 c.c. of nitric acid ( $d$  1.5), the solution was warmed, diluted with water, and basified, and the dinitro-compound was recrystallised; it formed golden plates, m. p.  $242$ – $244^{\circ}$ , identical with the specimen already described.

1-Nitrosoimino-2-ethyl-1 : 2-dihydrobenzthiazole, prepared from 5 g. of iminoethyldihydrobenzthiazole in glacial acetic acid (35 c.c.) and sodium nitrite (2.6 g.) in water (13 c.c.), separated from alcohol in orange-red plates (4–4.5 g.), which exploded at 153° (Found : N, by slow combustion with twice the usual amount of fine CuO, 20.5; S, 15.2.  $C_9H_9ON_3S$  requires N, 20.3; S, 15.5%).

1-Keto-2-ethyl-1 : 2-dihydrobenzthiazole.—The nitrosoiminoethyldihydrobenzthiazole (3 g.) in xylene (20 c.c.) was heated until nitrogen was no longer evolved and the xylene was removed. The oily residue was distilled in steam, and the distillate extracted with chloroform; the ketoethyldihydrobenzthiazole was a colourless refractive oil (1.3 g.) which could not be crystallised (Found : S, 17.2.  $C_9H_9ONS$  requires S, 17.8%).

The tetrabromide, obtained as in the case of the methyl derivative, formed unstable purple-brown crystals, m. p. 80–82° (turning yellow at 60–70°) (Found : Br, 64.2.  $C_9H_9ONBr_4S$  requires Br, 64.1%). 5-Bromo-1-keto-2-ethyl-1 : 2-dihydrobenzthiazole crystallised from absolute methyl alcohol in needles, m. p. 96–97° (Found : N, 5.6; Br, 30.8; S, 12.8.  $C_9H_8ONBrS$  requires N, 5.4; Br, 31.0; S, 12.4%).

*Synthesis of 5-Bromo-1-keto-2-ethyl-1 : 2-dihydrobenzthiazole from 5-Bromo-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole by Way of 5-Bromo-1-nitrosoimino-2-ethyl-1 : 2-dihydrobenzthiazole.*—5-Bromo-1-nitrosoimino-2-ethyl-1 : 2-dihydrobenzthiazole crystallised in salmon-pink plates, which exploded at 157–158° on being fairly rapidly heated (Found : Br, 27.4; S, 11.4.  $C_9H_8ON_3BrS$  requires Br, 27.6; S, 11.2%). The residue obtained by evaporation of a solution of the nitroso-derivative (4 g.) in xylene (25 c.c.), on recrystallisation from alcohol (animal charcoal), yielded 2.8 g. of 5-bromo-1-keto-2-ethyl-1 : 2-dihydrobenzthiazole, identical with that obtained above from the tetrabromide.

5-Nitro-1-keto-2-ethyl-1 : 2-dihydrobenzthiazole.—(i) 5-Nitro-1-nitrosoimino-2-ethyl-1 : 2-dihydrobenzthiazole, prepared from 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole, formed soft salmon-pink crystals, which exploded at 154° (Found : S, 12.5.  $C_9H_8O_3N_4S$  requires S, 12.7%). 5-Nitro-1-keto-2-ethyl-1 : 2-dihydrobenzthiazole, obtained by heating the nitrosoimino-compound (1 g.) in xylene (5 c.c.), separated from hot benzene in tufts of yellow needles, m. p. 198° (Found : S, 14.4.  $C_9H_8O_3N_2S$  requires S, 14.3%).

(ii) The 5-nitro-1-keto-derivative was also obtained in 80–90% yield by adding the 1-keto-2-ethyldihydro-derivative to nitric acid (*d* 1.5) (10 vols.) at 0–5°.

1-Thiol-2-ethyl-1 : 2-dihydrobenzthiazole.—A finely powdered, intimate mixture of 1-nitrosoimino-2-ethyl-1 : 2-dihydrobenzthiazole

(3 g.) and phosphorus pentasulphide (Kahlbaum) (3 g.) was heated in an oil-bath at  $120^{\circ}$ , a violent reaction taking place. The product was twice extracted with 50 c.c. of boiling benzene; the united extracts were boiled with copper turnings and filtered. The gum obtained by removal of the benzene crystallised from methyl alcohol in yellow plates, m. p.  $75^{\circ}$  (Found: S, 32.9.  $C_9H_9NS_2$  requires S, 32.8%).

*Nitration of 1-Imino-2-ethyl-1:2-dihydrobenzthiazole Hydrotribromide.*—The hydrotribromide (7 g.) was added to 60 c.c. of nitric acid ( $d$  1.5) at  $3-6^{\circ}$  in the course of 20 minutes; the solution was decanted from the liquid bromine which separated and poured into 250 c.c. of water. The filtrate from the precipitated nitrate, on basification, extraction with chloroform, and recrystallisation of the product from methyl alcohol, yielded 0.8 g. of 5-nitro-1-imino-2-ethyl-1:2-dihydrobenzthiazole. The precipitated nitrate, on decomposition with 20% alkali solution, yielded 2 g. of 5-bromo-3-nitro-1-imino-2-ethyl-1:2-dihydrobenzthiazole, which was identified by its m. p. and mixed m. p. and by the m. p. and mixed m. p. of its acetyl derivative.

*Decomposition of 1-Imino-2-ethyl-1:2-dihydrobenzthiazole Hydrotribromide by Sulphuric Acid.*—3 G. of the hydrotribromide were gradually added to 25 c.c. of 99% sulphuric acid at  $0-2^{\circ}$ ; hydrogen bromide was evolved and liquid bromine separated. The solution was poured on ice (200 g.), the mixture basified and extracted with chloroform, and the gum obtained by removal of the chloroform was acetylated with acetic anhydride (7 c.c.) and alcohol (15 c.c.). Fractional crystallisation of the product yielded 0.5 g. of 1-acetimido-2-ethyl-1:2-dihydrobenzthiazole and 0.7 g. of 5-bromo-1-acetimido-2-ethyl-1:2-dihydrobenzthiazole, which were identified by m. p. and mixed m. p. determinations.

*Nitration of 1-Imino-2-ethyl-1:2-dihydrobenzthiazole Hydrobromide.*—4 G. of the hydrobromide were gradually added to 50 c.c. of nitric acid ( $d$  1.5) at  $3-7^{\circ}$ , and the solution poured into 200 c.c. of water. The mixture was cooled to  $20^{\circ}$ , and the precipitated nitrate collected; the filtrate, on basification and extraction with chloroform, yielded 2.2 g. of 5-nitro-1-imino-2-ethyl-1:2-dihydrobenzthiazole. On decomposition with 20% alkali solution, the nitrate yielded 1.3 g. of 5-bromo-3-nitro-1-imino-2-ethyl-1:2-dihydrobenzthiazole, which was identified as in the previous case.

*Nitration of 1-Acetimido-2-ethyl-1:2-dihydrobenzthiazole.*—4 G. of the acetyl derivative were gradually added to 40 c.c. of nitric acid ( $d$  1.5) at  $0-2^{\circ}$ ; the temperature was allowed to rise to  $15^{\circ}$ , the mixture poured into 250 c.c. of water, and the precipitated nitro-derivative collected and extracted with 35 c.c. of boiling alcohol.

The residue (2.1 g.) had m. p. 240—242° (241—242° when mixed with 5-nitro-1-acetimido-2-ethyl-1 : 2-dihydrobenzthiazole); the alcoholic extract on evaporation yielded a small quantity of what appeared to be impure nitrate of 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole. Basification of the original acid filtrate yielded a further 1.9—2 g. of the 5-nitro-1-acetyl derivative.

*Nitration of 5-Bromo-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole.*—This was carried out at 0—5° in the usual way. 5-Bromo-3-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole formed orange needles, m. p. 168—169° (Found: N, 14.0; Br, 26.3; S, 10.4.  $C_9H_8O_2N_3BrS$  requires N, 13.9; Br, 26.4; S, 10.6%). The acetyl derivative crystallised from alcohol-ethyl acetate in pale yellow needles, m. p. 252—253° (Found: Br, 23.1.  $C_{11}H_{10}O_3N_3BrS$  requires Br, 23.2%). The nitrate separated from alcohol in yellow needles, m. p. 230° (decomp.).

Nitration of 5-bromo-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole hydrotribromide yielded solely 5-bromo-3-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole.

*Nitration of 1-Imino-2-ethyl-1 : 2-dihydrobenzthiazole in Sulphuric Acid Solution.*—The nitration of 5 g. of the base in 20 c.c. of 99% sulphuric acid at 70° with a mixture of nitric acid (*d* 1.4) (4 c.c.) and sulphuric acid (5 c.c.) gave 3.7 g. of impure 5-nitro-1-imino-2-ethyl-1 : 2-dihydrobenzthiazole, accompanied by a small quantity of the dinitro-derivative.

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## XXII.—*Nitration of 2'- and 4'-Nitro-1-phenyl-piperidines.*

By RAYMOND JAMES WOOD LE FÈVRE.

ORDINARY nitric acid (*d* 1.4) nitrates 4'-nitro-1-phenylpiperidine quantitatively in the 2'-position, but dissolves the 2'-nitro-isomeride unchanged. By the most extreme conditions of nitration under which the latter remains unaffected the former is destroyed.

Similar but less pronounced differences have been observed in the nitrations of 1 : 4-*di*(2'- and 4'-nitrophenyl)piperazines.

No such disparity is recorded in the literature concerning the conditions requisite for the production, by nitration of the corresponding mononitro-compounds with nitric acid of density not less than 1.42, of 2 : 4-dinitrodimethyl- or 2 : 4-dinitrodiethyl-aniline. An observation by Pinnow (*Ber.*, 1899, **32**, 1667), that dimethylaniline gave 95% of its weight of 2 : 4-dinitrodimethylaniline and 50% of its weight of 2-nitrodimethylaniline when treated with dilute sulphuric and nitric acids (see also Schuster and Pinnow, *Ber.*, 1896, **29**, 1053), would seem to indicate, however, that, of the initially formed *o*- and *p*-mononitro-compounds, only the latter underwent further nitration. Even were this so, the deductions from the present work would be unaffected, since the weakest nitrating acid used in the experiments on the nitrophenyl-piperidines was ordinary nitric acid (*d* 1.42). For comparison, it is now shown that the interaction of this reagent with 2-nitrodimethylaniline at room temperature leads to high yields of 2 : 4 : 6-trinitrophenylmethylnitroamine, and the observation of Weber (*Ber.*, 1877, **10**, 763), that by nitration of dimethylaniline with a solution of nitric acid in glacial acetic acid complete 2 : 4-dinitration is readily effected, has been verified experimentally.

Moreover, with regard to Pinnow's results, from general principles it would be expected that progressive dilution of the attacking reagent would render any slight difference in reactivity of two positions in a substituted benzene nucleus increasingly obvious, and the experiments of Clemo and Smith (*J.*, 1928, 2414) have shown that dilution of the nitrating acids with *water* is, in the case of certain dimethylanilines, a change of experimental conditions likely to lead to fundamentally different results.

The tendency of 2'- and 4'-nitro-1-phenylpiperidines to undergo salt formation is apparently strong; combination of either with mineral acid was violent (much more so than the analogous reactions with the nitrodimethylanilines) and each gave a stable *perchlorate*, *ferrichloride*, and *mercurichloride*.

An explanation of the present observations must therefore be sought in the relatively (to dialkyl) rigid structure of the piperidine ring, which, in the case, for example, of the *o*-nitro-compound, would more effectively (a) *spread* the area of direct influence of the

two positive charges  $\left[ \text{CH}_2 \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{N}^+ \begin{array}{c} \text{R} \\ \text{NO}_2 \end{array} \right] \text{X} \text{ (I)}$  by its

spatial interactions with the bulky *o*-nitro-group and (b) prevent the nearer approach of the negative anion  $\bar{\text{X}}$  and consequent reduction



of the strong inductive and direct effects set up by the positive poles indicated in (I) (compare Pollard and Robinson, J., 1927, 2770).

#### EXPERIMENTAL.

*Action of Nitric Acid on 2'-Nitro-1-phenylpyperidine.*—(a) When the nitro-compound (2 g.) was added cautiously and in portions to 10 c.c. of fuming nitric acid at the ordinary temperature, it dissolved with a hissing noise (addition of too large a portion caused inflammation). After 5 minutes, dilution with water and basification with ammonia gave nearly 2 g. of a bright red solid, m. p. 76—77° (alone, or mixed with authentic 2'-nitro-1-phenylpyperidine). (b) The nitro-compound (2 g.), after being dissolved in 10 c.c. of sulphuric acid, treated with 10 c.c. of fuming nitric acid, and heated on the water-bath for 15 minutes, was largely recovered unchanged; considerable decomposition, however, occurred.

*Action of Nitric Acid on 4'-Nitro-1-phenylpyperidine.*—The nitro-compound gave an uncrystallisable red oil under conditions (a) and was destroyed under conditions (b). When a solution of the nitro-compound (2 g.) in ordinary nitric acid (*d* 1.4) at 0° was left for 1 minute, then diluted with water and made alkaline, an almost quantitative yield of 2':4'-dinitro-1-phenylpyperidine, m. p. 92°, was obtained.

*Preparation of 1:4-Di(2'- and 4'-nitrophenyl)piperazines.*—Equal weights of the appropriate chloronitrobenzene and piperazine hydrate were gently boiled together for 15 minutes. The product was extracted repeatedly with boiling alcohol, and the residue crystallised. 1:4-Di(2'-nitrophenyl)piperazine separated in orange plates, m. p. 193—194°, from much glacial acetic acid (Found: N, 17.2.  $C_{16}H_{16}O_4N_4$  requires N, 17.1%), and the corresponding 4'-nitro-compound as a microcrystalline red powder, m. p. 263—264°, from phenol-nitrobenzene although the crude substance was yellow (Found: N, 17.2%).

*Nitration of 1:4-Di(2'- and 4'-nitrophenyl)piperazines.*—1 G. of each compound was dissolved in separate equal large volumes of hot acetic acid and 5 c.c. of nitric acid (*d* 1.5) were added. The production of 1:4-di(2':4':6'-trinitrophenyl)piperazine (Le Fèvre and Turner, J., 1927, 113) from the former compound was complete after the mixture had been kept at the ordinary temperature for 12 hours; in the case of the 4'-nitro-compound, 10 minutes were sufficient.

*Action of Nitric Acid on 2-Nitrodimethylaniline.*—This substance was prepared in good yield by 8 hours' boiling of a mixture of *o*-chloronitrobenzene (15 g.), 30% dimethylamine solution (35 g.), and sufficient alcohol to produce a homogeneous solution. The

product, after dilution with water, was extracted with benzene, and the extract washed with water and finally with dilute sulphuric acid. The acid solution was basified and again shaken with benzene. 2-Nitrodimethylaniline distilled at 145—155°/ca. 30 mm. as a clear red oil.

By addition of 1 g. to 15 c.c. of nitric acid ( $d$  1.42) at the ordinary temperature, followed after 15 minutes' solution by precipitation by dilution with water, a cream-coloured crystalline product was obtained, brief treatment of which with hot aqueous-alcoholic ammonia gave picramide, m. p. 188—189° (alone or mixed with an authentic specimen). Crystallisation of the nitration products from alcohol afforded cream plates, m. p. 131° (alone or mixed with authentic 2 : 4 : 6-trinitrophenylmethylnitroamine). Since 2 : 4-dinitrodimethylaniline is undoubtedly a precursor of "tetryl" in its direct formation from dimethylaniline, it is obvious that the 4-mononitration of 2-nitrodimethylaniline is a readily effected process and that 2-nitrodimethylaniline differs markedly from 2'-nitro-1-phenylpyperidine in this respect.

*Dinitration of Dimethylaniline.*—Dimethylaniline (12 g.; 1 mol.), dissolved in glacial acetic acid (80 g.), was slowly treated at 0—5° with fuming nitric acid (15 g.; 2 mols.) diluted with an equal volume of acetic acid. The resulting mixture was left until its temperature had risen to 15°; it was then diluted with much water. The yellow crystalline precipitate obtained, after drying, had m. p. ca. 75° (after two crystallisations from carbon disulphide the m. p. was 78.5—79.5°) and its weight (19 g.) corresponded to a 90% yield of 2 : 4-dinitrodimethylaniline.

*Complex Salts from 2'- and 4'-Nitro-1-phenylpyperidines.*—The two nitro-compounds dissolved readily in concentrated hydrochloric acid. To the solutions, slightly diluted with water, concentrated ferric chloride solution was added slowly. After filtration and crystallisation from acetic acid, 2'-nitro-1-phenylpyperidinium ferrichloride, dark yellow needles, m. p. 147—148° (Found: N, 7.0.  $C_{11}H_{15}O_2N_2Cl_4Fe$  requires N, 6.9%), and 4'-nitro-1-phenylpyperidinium ferrichloride, straw-yellow needles, m. p. 130—135°, were obtained. No ferrichloride formation could be observed with 2' : 4'-dinitro-1-phenylpyperidine.

Addition of aqueous mercuric chloride to the above hydrochloric acid solutions gave the corresponding mercurichlorides, which formed cream-coloured plates, m. p. 170—175°, and bright yellow plates, m. p. 70—80°, respectively.

Addition of aqueous perchloric acid to mineral acid solutions of 2'-nitro-1-phenylpyperidine precipitated a white microcrystalline perchlorate which, after crystallisation from glacial acetic acid, had

m. p. 240—243° (decomp.) (Found : N, 9.3.  $C_{11}H_{15}O_6N_2Cl$  requires N, 9.15%). The corresponding 4'-nitro-1-phenylpiperidinium perchlorate was apparently soluble in water, since a hydrochloric acid solution of 4'-nitro-1-phenylpiperidine could, after addition of aqueous perchloric acid, be diluted with a large excess of water without any precipitation occurring.

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### XXIII.—*Sugar Carbonates. Part IV. The Dicarbonates of Glucose, Fructose, Mannose, Galactose, and Arabinose.*

By WALTER NORMAN HAWORTH and CHARLES RAYMOND PORTER.

A SERIES of new crystalline derivatives of sugars has been prepared

containing two carbonate residues of the type  $\begin{array}{c} \text{CH}-\text{O} \\ | \quad \diagup \\ \text{CH}-\text{O} \end{array} \text{CO}.$

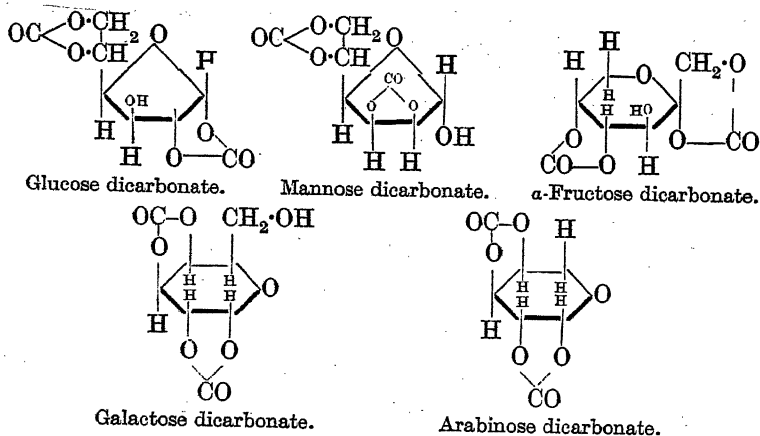
Hitherto the attempts to prepare these substances have led either to the introduction of only one such residue or to the formation of sugar carbonates containing also carbonic ester groups. The present results have been obtained by the condensation of various sugars with carbonyl chloride in pyridine solution. Accompanying the crystalline dicarbonate there is usually an amorphous by-product of higher molecular weight which appears to be a polysaccharide derivative. The latter reaction has not been studied in detail.

The dicarbonates of the sugars are well-defined and easily characterised products which resemble closely the diacetone derivatives of the sugars. For instance, they are hydrolysed by dilute acids to the parent sugars; this change, however, does not proceed nearly so readily as with the sugar-acetones. On the other hand, the sugar carbonates are instantly attacked by alkali even in the cold. It is these properties that suggested the utilisation of the dicarbonates in synthetic operations such as those recently described (J., 1929, 2796).

The specific rotations of the dicarbonates derived from glucose, fructose, and mannose are analogous to those of the corresponding diacetone derivatives, but arabinose dicarbonate,  $[\alpha]_{5780} + 61.3^\circ$ , and galactose dicarbonate,  $[\alpha]_{5780} - 86.5^\circ$ , have higher rotations than arabinose-diacetone and galactose-diacetone,  $[\alpha]_{5780} \pm 1^\circ$  and  $-56^\circ$  respectively (in aqueous acetone). These variations appear to be due to differences of conformation rather than of structure.

The constitutional formulæ suggested are indicated below and

are based on the similarity in properties to the diacetones, the constitutional formulæ of which have been elucidated.



Evidence of the constitution here assigned to mannose dicarbonate is furnished by the fact that this substance gives rise to a crystalline anilide and a crystalline methylmannoside dicarbonate which does not reduce Fehling's solution. This interesting mannoside will form the subject of a further communication.

The behaviour of the glucose dicarbonate, including its relationship to glucose-acetone carbonate (*loc. cit.*), provides support for the constitution which is here assigned.

#### EXPERIMENTAL.

*Glucose Dicarbonate.*—In the first attempts to condense carbonyl chloride with glucose the sugar was dissolved in pyridine, cooled in ice, and vigorously stirred while a 20% solution of carbonyl chloride in toluene was added drop by drop. The addition caused the precipitation of a yellow crystalline solid (possibly the addition compound of carbonyl chloride and pyridine), and the removal of the reagent in this form was probably the reason for the minute amount of sugar carbonate formed in this way.

In subsequent experiments gaseous carbonyl chloride, obtained from a cylinder of the compressed gas, was passed into the solution of the sugar in pyridine. At the end of the reaction the mixture was treated with ice, to decompose the carbonyl chloride-pyridine complex, and the liquid was filtered. When the reaction was arrested after about an hour, an almost clear solution was obtained, but if the reagents had been in contact for several hours, or if a very rapid current of carbonyl chloride had been passed, or the temperature allowed to rise, a considerable amount of an insoluble

amorphous condensation product (A) was formed, which was removed by filtration.

The aqueous filtrate contained pyridine, pyridine hydrochloride, glucose dicarbonate, and glucose. The pyridine and its hydrochloride were removed together by adding an excess of barium carbonate and evaporating the solution to a small bulk at 30—35° under reduced pressure. The glucose dicarbonate was sparingly soluble in water and was extracted with ethyl acetate in a mechanical extractor. Another and somewhat more rapid method of separating the sugar carbonate from the original mixture consisted in treatment of the latter with excess of barium carbonate and repeated extraction with ethyl acetate: the whole of the pyridine was thus removed, and with it the sugar carbonate, which was much more soluble in pyridine than in ethyl acetate. The latter solvent was eliminated by distillation at 40—50° under diminished pressure. The residual pyridine solution was evaporated at the ordinary temperature in a vacuum desiccator containing sulphuric acid. The residue was a viscid liquid or glassy solid, which became crystalline on trituration with alcohol. In this method, some unchanged glucose as well as the glucose carbonate was extracted by the pyridine.

In a typical preparation, carbonyl chloride was passed for 1 hour, from a delivery tube with a bell-shaped orifice in order to prevent stoppages, into an ice-cooled, vigorously stirred solution of 18 g. of glucose in about 50 c.c. of pyridine. The product was treated with ice-water, filtered, and extracted with ethyl acetate. During the extraction, sufficient barium carbonate was added to neutralise the hydrochloric acid liberated by the removal of pyridine from the solution of its hydrochloride. Evaporation of the solvents from this extract left a viscid mass which deposited crystals on treatment with alcohol. Further crops of crystals were deposited on concentration of the alcoholic solution, and finally a viscid residue remained which yielded no further crystalline material (yield, 1 g.).

An attempt was also made to prepare a glucose carbonate by passing carbonyl chloride into a thoroughly stirred, concentrated aqueous solution of glucose cooled in ice and salt. The hydrochloric acid and excess of carbonyl chloride were then removed by the addition of silver carbonate, and the solution was evaporated at a low temperature. The product crystallised and appeared to be mainly unchanged glucose; a very small amount of glucose carbonate was, however, detected.

The amorphous product A (see above) was insoluble in the usual organic solvents except pyridine, but was soluble in a mixture of acetone and water. It gave a precipitate of barium carbonate when warmed with barium hydroxide solution, and reduced Feh-

ling's solution. On treatment with dilute alkali it dissolved, a polysaccharide being probably formed.

*Glucose dicarbonate* is sparingly soluble in most solvents, the decreasing order of solubility being pyridine, acetone (about 1.5% in cold), ethyl acetate, alcohol (about 0.4% when boiling), water, and chloroform. It crystallises well from alcohol, being about four times as soluble in the hot as in the cold, yielding needles or lustrous flakes, m. p.  $224^{\circ}$  (efferv.; sintering at  $200^{\circ}$ ).

Glucose dicarbonate is hydrolysed rapidly by dilute alkalis, but is not readily decomposed by dilute acids in the cold. When it is warmed with aqueous barium hydroxide solution, a precipitate of barium carbonate is formed. The alkali present in Fehling's solution is sufficient to effect hydrolysis, followed by reduction. The dicarbonate has  $[\alpha]_D - 29^{\circ}$  ( $c = 1.0$  in acetone containing 25% of water). No change in this value was observed, even after the addition of a drop of aqueous hydrochloric acid (Found: C, 41.5; H, 3.6;  $\text{CO}_2$ , 37.5;  $M$ , ebullioscopic in acetone, 239.  $\text{C}_8\text{H}_8\text{O}_8$  requires C, 41.4; H, 3.5;  $\text{CO}_2$ , 37.9%;  $M$ , 232).

*Galactose Dicarbonate*.—This compound was prepared in the same manner as glucose dicarbonate. Several variations of the method of extraction were tried, but the process ultimately adopted for the glucose analogue was found to be the most effective.

In general, *galactose dicarbonate* is similar in its properties to glucose dicarbonate. It is, however, somewhat more soluble in water, from which it crystallises well in long needles, m. p.  $212^{\circ}$  (efferv.; slight sintering at  $190^{\circ}$ );  $[\alpha]_{D}^{21.3} - 86.5^{\circ}$  in acetone containing 25% of water ( $c = 0.6$ ). The addition of a trace of hydrochloric acid did not alter the rotation in 22 hours (Found: C, 41.7; H, 3.7.  $\text{C}_8\text{H}_8\text{O}_8$  requires C, 41.4; H, 3.5%).

*Mannose Dicarbonate*.—This preparation proceeded rather more readily than in the previous examples, and the product was more easily extracted.

In a typical preparation, 6 g. of mannose were dissolved in 20 c.c. of pyridine, the solution was cooled in an ice-bath and vigorously stirred, and a fairly rapid current of carbonyl chloride was passed for about  $\frac{3}{4}$  hour. Ice-water was then added, and 1.5 g. of an amorphous carbonate, probably a polysaccharide carbonate, were collected. The filtrate was treated with an excess of barium carbonate and evaporated to small bulk under diminished pressure at  $30-35^{\circ}$ . After removal of the pyridine by this process, the solution was filtered and extracted with ethyl acetate in the mechanical extractor. Yield, 0.5 g.

*Mannose dicarbonate* crystallised well from water in lustrous flakes or needles, m. p.  $122-123^{\circ}$  (efferv.; slight sintering at  $118^{\circ}$ ).

It gave a precipitate with barium hydroxide solution, and reduced Fehling's solution suddenly, on heating (Found: C, 41.4; H, 3.6;  $\text{CO}_2$ , 36.7.  $\text{C}_8\text{H}_8\text{O}_8$  requires C, 41.4; H, 3.5;  $\text{CO}_2$ , 37.9%).  $[\alpha]_{5780}^{25} + 26^\circ$ ;  $[\alpha]_{5461}^{21} + 28.5^\circ$  in dry acetone ( $c = 1.0$ ). The substance showed no appreciable mutarotation in this solvent even after the addition of a trace of hydrochloric acid.

The *anilide* of mannose dicarbonate was prepared by heating mannose dicarbonate and aniline (2 mols.) in alcoholic solution for 2 hours. The solution was then allowed to evaporate at the ordinary temperature. The residue, after being triturated with several solvents, crystallised from ethyl acetate, containing dry ether, in hard white prisms, m. p.  $174\text{--}175^\circ$ . The substance was sparingly soluble in alcohol or ethyl acetate and slowly became discoloured on exposure to the air.  $[\alpha]_{5780}^{30} - 70^\circ$  (after 5 minutes);  $-32^\circ$  (after 18 hours) in ethyl alcohol ( $c = 0.2$ );  $[\alpha]_D^{18} - 83^\circ$  in methyl alcohol ( $c = 0.1$ ) (Found: C, 54.85; H, 4.5; N, 4.65.  $\text{C}_{14}\text{H}_{13}\text{O}_7\text{N}$  requires C, 54.7; H, 4.25; N, 4.55%).

*Fructose Dicarbonate*.—Fructose (10 g.) was dissolved in 25 c.c. of pyridine and cooled in ice and vigorously stirred. A fairly rapid current of carbonyl chloride was admitted during  $\frac{3}{4}$  hour; ice-water was then added, and an amorphous fructose carbonate derivative removed by filtration. After addition of excess of barium carbonate, the filtrate was extracted with ethyl acetate, first by hand and then mechanically. The ethyl acetate was distilled at  $40\text{--}50^\circ$  under slightly reduced pressure and the pyridine was evaporated from the residue at the ordinary temperature in a vacuum desiccator containing sulphuric acid. When only a trace of pyridine remained, a little water was added, which caused the fructose dicarbonate to become crystalline (yield, 1 g.).

The aqueous solution remaining after the extraction with ethyl acetate was evaporated to dryness at  $30\text{--}35^\circ$ , and the finely powdered residue extracted repeatedly with boiling acetone in the hope of isolating an isomeric fructose dicarbonate. Only a small amount of a syrupy product was extracted and this yielded a further amount of the same fructose dicarbonate.

*Fructose dicarbonate* has solubilities intermediate between those of the corresponding derivatives of glucose and mannose, being quite easily soluble in acetone and alcohol. It crystallised well from water, separating in hard prisms if not quite pure, but when pure it was obtained in clusters of needles. It contained  $\frac{1}{2}$  mol. of water of crystallisation, which was not removed in a vacuum over sulphuric acid at the ordinary temperature, but was eliminated in a vacuum at  $90^\circ$ . M. p.  $173\text{--}174^\circ$ ; effervescence occurred at this temperature after a few seconds. The rotation was similar to that

of the  $\alpha$ -form of fructose diacetone, and mutarotation was not observed on the addition of a trace of hydrochloric acid.  $[\alpha]_{5780}^{16^\circ} - 143^\circ$  and  $[\alpha]_{5461}^{16^\circ} - 159^\circ$  (in 50% aqueous acetone,  $c = 1.14$ ) (Found: C, 40.1; H, 3.95;  $\text{CO}_2$ , 36.4;  $\text{H}_2\text{O}$ , 3.4.  $\text{C}_8\text{H}_8\text{O}_8 \cdot \frac{1}{2}\text{H}_2\text{O}$  requires C, 39.9; H, 3.75;  $\text{CO}_2$ , 36.5;  $\text{H}_2\text{O}$ , 3.7%).

The amorphous substance which was collected after the addition of ice-water to the pyridine solution in the above reaction appeared to be insoluble in most liquids except pyridine, but was soluble in acetone containing a little water. The acetone was allowed to evaporate from such a solution and the precipitated solid was removed. The aqueous filtrate left only a small amount of glassy residue on evaporation. The precipitated solid was washed with water and was then almost completely soluble in dry acetone. It was extracted with this solvent, and the solution allowed to evaporate; the vitreous residue became opaque on trituration with water. It reduced Fehling's solution, and gave a precipitate when warmed with barium hydroxide solution. The product decomposed without melting between  $150^\circ$  and  $180^\circ$ .  $[\alpha]_{5780}^{15^\circ} - 58^\circ$  ( $c = 1.29$  in acetone) (Found:  $\text{CO}_2$ , 37.7%;  $M$ , ebullioscopic in acetone, 780, 765). This molecular weight is intermediate between those required by three (660) and four (874) fructose dicarbonate residues joined by loss of water. The carbonate values required by these substances are 40.0 and 40.3% respectively.

A further attempt was made to separate the obviously complex mixture by fractional precipitation from acetone solution by the addition of ether. By this process four fractions were collected, the rotations of which did not vary greatly [(1)  $[\alpha]_{5780} - 64^\circ$ ; (2)  $[\alpha]_{5780} - 58.5^\circ$ ; (3)  $[\alpha]_{5780} - 63^\circ$ ; (4)  $[\alpha]_{5780} - 65^\circ$ ], and, although the solubilities of the fractions differed considerably, pure substances were not obtained. The examination of this mixture is therefore held over until larger quantities are available.

*Arabinose Dicarbonate.*—The reaction of arabinose with carbonyl chloride in pyridine did not proceed so quickly as was the case with the other sugars. The gas was passed for 2 hours into a cooled and vigorously stirred solution of 10 g. of arabinose in 30 c.c. of pyridine. The product was an extremely thick paste, and stirring was impracticable. Ice-water was added, and the clear solution extracted with ethyl acetate, barium carbonate being added to keep the solution neutral. After removal of the solvent from the extracts as in previous cases, a viscid syrup remained which deposited crystals on treatment with water. The filtrate from this solid deposited more crystalline material after being kept for some weeks (yield, 2 g.).

*Arabinose dicarbonate* is slightly soluble in chloroform, but rather more soluble in ethyl acetate, alcohol, water, and acetone. It



crystallises well from water (solubility in hot water, 1 part in 140 parts). It separated in short hard prisms when not quite pure, and in longer crystals when pure. M. p. 200—202° (efferv.). It gave a precipitate with barium hydroxide and reduced Fehling's solution.

When heated to 160° in a vacuum, this dicarbonate very slowly sublimes, and at a slightly higher temperature, *e.g.*, 180—190°, can be economically purified by this procedure. This behaviour is in marked contrast to that of the dicarbonates of the hexoses, which appeared to possess a negligible vapour pressure and decomposed on prolonged heating.

Arabinose dicarbonate did not exhibit mutarotation in aqueous acetone, even after the addition of a trace of hydrochloric acid.  $[\alpha]_{D}^{25} + 61.3^{\circ}$ ;  $[\alpha]_{D}^{25} + 66.0^{\circ}$  (in acetone containing 33% of water,  $c = 1.3$ ) (Found: C, 41.7; H, 3.1; CO<sub>2</sub>, 41.6. C<sub>7</sub>H<sub>8</sub>O<sub>7</sub> requires C, 41.6; H, 3.0; CO<sub>2</sub>, 43.5%).

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## XXIV.—*The Action of Bromine upon the p-Tolylhydrazones of Benzaldehyde and of the Nitrobenzaldehydes.*

By FREDERICK DANIEL CHATTAWAY and ARTHUR B. ADAMSON.

BROMINE reacts very readily with the *p*-tolylhydrazones of benzaldehyde and of the nitrobenzaldehydes.

When 2 mols. of bromine are allowed to act upon 1 mol. of any one of the hydrazones, one atom of bromine enters the *p*-tolyl nucleus in an *o*-position with respect to the nitrogen atom and a second the  $\omega$ -position.

The action of 1 mol. of bromine upon 1 mol. of hydrazone yields a mixture of the  $\omega\omega$ -dibromo-derivative and unchanged hydrazone.

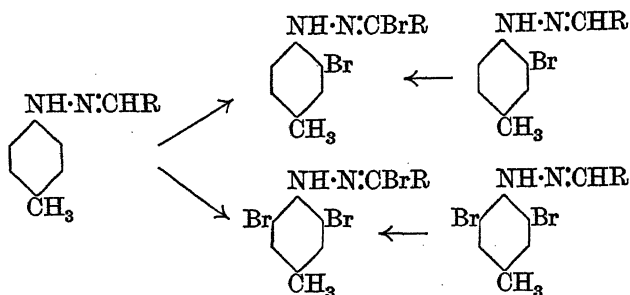
The  $\omega\omega$ -dibromo-hydrazones are also obtained by the action of 1 mol. of bromine upon the hydrazones of 3-bromo-*p*-tolylhydrazine.

When a large excess of bromine is used, a third atom of bromine can be introduced into the remaining *o*-position in the *p*-tolyl nucleus. A larger excess of halogen is required to effect complete tribromination of benzaldehyde- and *p*-nitrobenzaldehyde-*p*-tolylhydrazones than of *m*-nitrobenzaldehyde-*p*-tolylhydrazone.

Compounds containing more than three atoms of bromine in the

molecule cannot be obtained by the direct bromination of these hydrazones.

The course of the reactions may be represented thus :



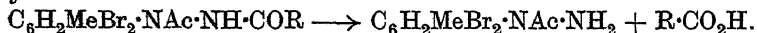
In these  $\omega$ -bromo-hydrazones the  $\omega$ -bromine atom is very reactive. When heated with sodium acetate and acetic acid, they are converted into the corresponding  $\beta$ -acetyl-hydrazides of benzoic or nitrobenzoic acid :



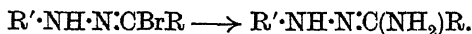
These hydrazides may be hydrolysed with aqueous-alcoholic hydrochloric acid, a substituted *p*-tolylhydrazine and an acid corresponding to the aldehyde forming the original hydrazone being produced. When only one *o*-bromine atom is present in the *p*-tolyl nucleus, the  $\beta$ -acetyl group of the hydrazide is removed by hydrolysis



but when both *o*-positions are occupied by bromine atoms, this acetyl group is protected and an  $\alpha$ -acetylated dibromo-*p*-tolylhydrazine is obtained :



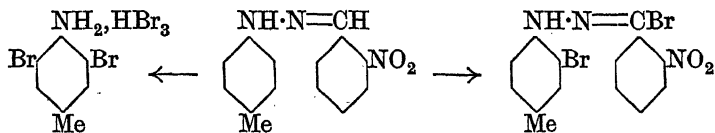
The  $\omega$ -bromo-hydrazones are converted into the corresponding hydrazidines by the action of concentrated aqueous ammonia :



These are highly-coloured weak bases and form colourless crystalline hydrochlorides which are rather unstable and sparingly soluble in alcohol or dilute hydrochloric acid.

*o*-Nitrobenzaldehyde-*p*-tolylhydrazone does not behave in quite the same way as its isomerides, this hydrazone being rather less stable. When 2 mols. of bromine are used, an  $\omega$ -bromo-compound is obtained in the normal manner. A larger proportion of bromine has no further action at the ordinary temperature, but when the temper-

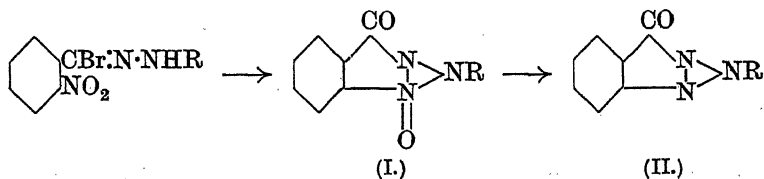
ature is allowed to rise, the hydrazone breaks down and the bright orange *perbromide* of 3 : 5-dibromo-*p*-toluidine is formed :



Although not produced by the direct bromination of *o*-nitrobenzaldehyde-*p*-tolylhydrazone,  $\omega$ -bromo-*o*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone is readily obtained by brominating *o*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone, the  $\omega$ -position being easily substituted.

The  $\omega$ -bromo-compounds derived from *o*-nitrobenzaldehyde-*p*-tolylhydrazone have different properties from those derived from other *p*-tolylhydrazones and readily lose hydrogen bromide, forming the violently explosive ketoendoaryliminodihydrobenzisodiazole oxides (I) (the so-called isodiazomethane derivatives) (J., 1925, 127, 2407).

This loss takes place even on cautious recrystallisation from alcohol. When boiled for several hours with alcohol, the explosive compounds lose one atom of oxygen and form ketoendoaryliminodihydrobenzisodiazole derivatives (II) (J., 1927, 323).



If bromination is carried out in the presence of sodium acetate, the formation of the  $\omega$ -bromo-compound and the elimination of hydrogen bromide from this take place successively and the explosive compound is obtained as the product of the one operation (J., 1925, 127, 2408).

When *o*-nitrobenzaldehyde-*p*-tolylhydrazone is brominated in the presence of sodium acetate, no substitution occurs in the *p*-tolyl nucleus at the ordinary temperature, even when excess of bromine is used, and consequently the explosive compound formed under these conditions contains no halogen.

#### EXPERIMENTAL.

$\omega$ -Bromo-*m*-nitrobenzaldehyde-3-bromo-*p*-tolylhydrazone.—To a suspension of 5 g. (1 mol.) of *m*-nitrobenzaldehyde-*p*-tolylhydrazone in 70 c.c. of acetic acid was slowly added a solution of 2.1 c.c. (2 mols.)

of bromine in 10 c.c. of acetic acid. The hydrazone dissolved, forming an orange solution from which  $\omega$ -bromo-*m*-nitrobenzaldehyde-3-bromo-*p*-tolylhydrazone separated as a bright yellow solid. After being washed with water, this crystallised from acetic acid, in which it was moderately easily soluble, in long, slender, bright yellow prisms, m. p.  $145.5^\circ$  (Found: Br, 39.1.  $C_{14}H_{11}O_2N_3Br_2$  requires Br, 38.7%).

$\omega$ -Bromo-*m*-nitrobenzaldehyde-3:5-dibromo-*p*-tolylhydrazone.—A solution of 3.1 c.c. (3 mols.) of bromine in 10 c.c. of acetic acid was added to a suspension of 5 g. (1 mol.) of *m*-nitrobenzaldehyde-*p*-tolylhydrazone in 100 c.c. of the same solvent. The dibromo-compound separated as a bright yellow solid, which became paler as it was converted into the tribromo-compound. The mixture was heated on a water-bath to complete the reaction and cooled, and the solid collected.  $\omega$ -Bromo-*m*-nitrobenzaldehyde-3:5-dibromo-*p*-tolylhydrazone crystallises from acetic acid, in which it is moderately easily soluble, in pale yellow prisms, m. p.  $154.5^\circ$  (Found: Br, 48.8.  $C_{14}H_{10}O_2N_3Br_3$  requires Br, 48.8%).

The same compound was easily prepared by the action of 1 mol. of bromine upon *m*-nitrobenzaldehyde-3:5-dibromo-*p*-tolylhydrazone.

$\omega$ -Bromo-*p*-nitrobenzaldehyde-3-bromo-*p*-tolylhydrazone.—This was obtained in a similar manner by the action of 2.1 c.c. (2 mols.) of bromine upon 5 g. (1 mol.) of *p*-nitrobenzaldehyde-*p*-tolylhydrazone suspended in 100 c.c. of acetic acid. It crystallised from acetic acid, in which it was moderately easily soluble, as a felted mass of bright orange needles, m. p.  $176^\circ$  (Found: Br, 39.1.  $C_{14}H_{11}O_2N_3Br_2$  requires Br, 38.7%).

$\omega$ -Bromo-*p*-nitrobenzaldehyde-3:5-dibromo-*p*-tolylhydrazone.—When 3 mols. of bromine were used to 1 mol. of *p*-nitrobenzaldehyde-*p*-tolylhydrazone, the product was almost exclusively  $\omega$ -bromo-*p*-nitrobenzaldehyde-3-bromo-*p*-tolylhydrazone. Not until 8 mols. of bromine were used was there any appreciable formation of the tribromo-compound and to ensure complete tribromination it was found advisable to use a still larger excess of bromine.

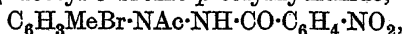
5 G. of *p*-nitrobenzaldehyde-*p*-tolylhydrazone (1 mol.) were suspended in 100 c.c. of acetic acid, and 10 c.c. (excess) of bromine added with vigorous shaking. The mixture was heated on a water-bath for 30 minutes to complete the reaction.  $\omega$ -Bromo-*p*-nitrobenzaldehyde-3:5-dibromo-*p*-tolylhydrazone, which separated as an orange solid, crystallised from acetic acid, in which it was easily soluble, in long orange-yellow prisms, m. p.  $161^\circ$  (Found: Br, 48.7.  $C_{14}H_{10}O_2N_3Br_3$  requires Br, 48.8%).

$\omega$ -Bromobenzaldehyde-3-bromo-*p*-tolylhydrazone.—This was obtained

by the action of 2.5 c.c. (2 mols.) of bromine upon 5 g. (1 mol.) of benzaldehyde-*p*-tolylhydrazone suspended in 25 c.c. of acetic acid. It crystallised from hot alcohol, in which it was easily soluble, in long colourless needles, m. p. 74° (Found: Br, 43.8.  $C_{14}H_{12}N_2Br_2$  requires Br, 43.5%).

*ω*-Bromobenzaldehyde-3:5-dibromo-*p*-tolylhydrazone.—This could be prepared from benzaldehyde-*p*-tolylhydrazone only by the use of a large excess of bromine. 10 C.c. of bromine were added to 5 g. of the hydrazone in 25 c.c. of acetic acid. The product crystallised from hot acetic acid, in which it was easily soluble, in long colourless needles, m. p. 106° (Found: Br, 53.8.  $C_{14}H_{11}N_2Br_3$  requires Br, 53.7%).

*m*-Nitrobenz-β-acetyl-3-bromo-*p*-tolylhydrazide,



was obtained as a white viscid solid which could not be made to crystallise. Its constitution was shown by hydrolysis with alcohol and hydrochloric acid; it then yielded acetic acid, *m*-nitrobenzoic acid, and 3-bromo-*p*-tolylhydrazine.

*m*-Nitrobenz-β-acetyl-3:5-dibromo-*p*-tolylhydrazide crystallised from alcohol in fine colourless prisms, m. p. 170° (Found: Br, 33.8.  $C_{16}H_{13}O_4N_3Br_2$  requires Br, 33.9%). On hydrolysis it yielded *m*-nitrobenzoic acid and α-acetyl-3:5-dibromo-*p*-tolylhydrazine. The latter was identified by conversion into its *m*-nitrobenzaldehydehydrazone, which crystallised from acetic acid in colourless shining plates, m. p. 218°, and was identical with the compound prepared by the action of acetic anhydride upon *m*-nitrobenzaldehyde-3:5-dibromo-*p*-tolylhydrazone.

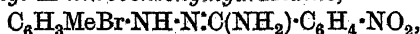
*p*-Nitrobenz-β-acetyl-3-bromo-*p*-tolylhydrazide crystallised from alcohol in colourless prisms, m. p. 173° (Found: Br, 20.6.  $C_{16}H_{14}O_4N_3Br$  requires Br, 20.4%). On hydrolysis it yielded acetic acid, *p*-nitrobenzoic acid, and 3-bromo-*p*-tolylhydrazine.

*p*-Nitrobenz-β-acetyl-3:5-dibromo-*p*-tolylhydrazide crystallised from alcohol in colourless prisms, m. p. 183° (Found: Br, 33.7.  $C_{16}H_{13}O_4N_3Br_2$  requires Br, 33.9%). On hydrolysis it yielded *p*-nitrobenzoic acid and α-acetyl-3:5-dibromo-*p*-tolylhydrazine.

*Benz*-β-acetyl-3:5-dibromo-*p*-tolylhydrazide crystallised from alcohol in colourless prisms, m. p. 190° (Found: Br, 37.4.  $C_{16}H_{14}O_2N_2Br_2$  requires Br, 37.5%). On hydrolysis it yielded benzoic acid and α-acetyl-3:5-dibromo-*p*-tolylhydrazine.

The following hydrazidines were prepared by the action of 5 c.c. of concentrated aqueous ammonia upon a suspension of 5 g. of the *ω*-bromo-compounds in 50 c.c. of alcohol.

3-Bromo-*p*-tolyl-*m*-nitrobenzenylhydrazidine,



crystallises from alcohol in red prisms, m. p.  $136^{\circ}$  (Found: Br, 22.8.  $C_{14}H_{13}O_2N_4Br$  requires Br, 22.9%). It forms a hydrochloride which crystallises from alcohol and hydrochloric acid in colourless plates, m. p.  $230^{\circ}$  (decomp.).

3 : 5-Dibromo-*p*-tolyl-*m*-nitrobenzenylhydrazidine crystallises from alcohol in yellow prisms, m. p.  $151^{\circ}$  (Found: Br, 37.6.  $C_{14}H_{12}O_2N_4Br_2$  requires Br, 37.4%), 3-bromo-*p*-tolyl-*p*-nitrobenzenylhydrazidine in deep purple prisms, m. p.  $155^{\circ}$  (Found: Br, 22.8.  $C_{14}H_{13}O_2N_4Br$  requires Br, 22.9%), and 3 : 5-dibromo-*p*-tolyl-*p*-nitrobenzenylhydrazidine in orange-yellow rhombic plates, m. p.  $145^{\circ}$  (Found: Br, 37.2.  $C_{14}H_{12}O_2N_4Br_2$  requires Br, 37.4%).

*The Bromination of o-Nitrobenzaldehyde-p-tolylhydrazone.*

$\omega$ -Bromo-*o*-nitrobenzaldehyde-3-bromo-*p*-tolylhydrazone.—2.1 C.c. of bromine (2 mols.) were added to 5 g. (1 mol.) of *o*-nitrobenzaldehyde-*p*-tolylhydrazone suspended in 50 c.c. of acetic acid. A dark brown solution was formed from which  $\omega$ -bromo-*o*-nitrobenzaldehyde-3-bromo-*p*-tolylhydrazone slowly separated in yellow crystals. Recrystallised from acetic acid, it formed yellow rhombic plates, m. p.  $105^{\circ}$  (decomp.). The recrystallisation must be rapidly effected, since the compound quickly decomposes when heated with acetic acid (Found: Br, 38.3.  $C_{14}H_{11}O_2N_3Br_2$  requires Br, 38.7%).

The compound cannot be recrystallised from alcohol, as it then loses hydrogen bromide and is converted into the highly explosive 3-keto-1 : 2-endo-3'-bromo-*p*-tolylimino-2 : 3-dihydro-1 : 2-benzisodiazole 1-oxide (I;  $R = C_6H_3MeBr$ ). This crystallises from alcohol in bright yellow, rhombic plates, explosion point  $139^{\circ}$  (Found: Br, 24.0.  $C_{14}H_{10}O_2N_3Br$  requires Br, 24.1%).

When 2 g. of the explosive compound were boiled for 2 hours under reflux with 25 c.c. of alcohol, a brown solution was obtained which, on cooling, deposited 3-keto-1 : 2-endo-3'-bromo-*p*-tolylimino-2 : 3-dihydro-1 : 2-benzisodiazole. This crystallised from alcohol in pale yellow prisms, m. p.  $166^{\circ}$  (Found: Br, 25.2.  $C_{14}H_{10}ON_3Br$  requires Br, 25.3%).

*The Action of Excess of Bromine upon o-Nitrobenzaldehyde-p-tolylhydrazone.*—5 G. of the hydrazone were suspended in 100 c.c. of acetic acid, and 10 c.c. of bromine added. A dark brown solution was formed from which, on shaking and cooling, 3 : 5-dibromo-*p*-toluidine perbromide separated. This, recrystallised from a 16% solution of bromine in acetic acid, formed bright orange prisms, m. p.  $134^{\circ}$  (decomp.) (Found: Br, 78.2.  $C_7H_8NBr_5$  requires Br, 79.0%).

This perbromide is fairly stable in the solid state and can be dried at  $100^{\circ}$  with only slight decomposition. It loses bromine and

hydrogen bromide on being washed with water or kept for several weeks over lime in a vacuum desiccator. It is easily soluble in acetic acid and when the solution is boiled, bromine is evolved; on cooling, 3 : 5-dibromo-*p*-toluidine separates in colourless needles, m. p. 73°.

The perbromide was also prepared by the action of an excess of bromine upon a solution of *p*-toluidine in acetic acid.

$\omega$ -Bromo-*o*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone was obtained by the action of 1 mol. of bromine upon *o*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone. It decomposes very readily when warmed with acetic acid, but can be recrystallised from a mixture of benzene and high-boiling petroleum, from which it separates in pale yellow prisms, m. p. 123° (decomp.) (Found: Br, 48.3.  $C_{14}H_{10}O_2N_3Br_3$  requires Br, 48.8%).

When boiled for a few minutes with alcohol, it loses hydrogen bromide and is converted into the highly explosive 3-keto-1 : 2-endo-3' : 5'-dibromo-*p*-tolylimino-2 : 3-dihydro-1 : 2-benzisodiazole 1-oxide, which crystallises from alcohol in bright yellow, rhombic plates, explosion point 167° (Found: Br, 39.1.  $C_{14}H_9O_2N_3Br_2$  requires Br, 38.9%).

The explosive compound (2 g.), when boiled with 25 c.c. of alcohol for 6 hours, gives the corresponding endoaryliminobenzisodiazole derivative, which crystallises from alcohol in yellow rhombic plates, m. p. 190° (decomp.).

*Bromination of o-Nitrobenzaldehyde-p-tolylhydrazone in the Presence of Sodium Acetate.*—5 G. of this hydrazone and 5 g. of anhydrous sodium acetate were suspended in 50 c.c. of acetic acid, and 1.1 c.c. of bromine (1 mol.) added. A dark solution was formed from which crystals of the explosive 3-keto-1 : 2-endo-*p*-tolylimino-2 : 3-dihydro-1 : 2-benzisodiazole 1-oxide slowly separated. It crystallised from alcohol in bright yellow prisms, explosion point 143°. The same compound, containing no halogen, was obtained even when 2 or 3 mols. of bromine were used at the ordinary temperature.

*Second Liversidge Lecture.*

DELIVERED BEFORE THE CHEMICAL SOCIETY ON DECEMBER 12TH,  
1929.

By HERBERT FREUNDLICH.

*Surface Forces and Chemical Equilibrium.*

I INTEND to discuss a problem of surface chemistry. It is well known that surface reactions are of the greatest importance in technical and biological processes. But these reactions are generally very complicated and it is therefore worth while to examine what we know about the simple case of a chemical equilibrium being influenced by surface forces.

J. J. Thomson ("Applications of Dynamics to Physics and Chemistry," London, 1888, p. 234) was the first to point out that a chemical equilibrium ought to be influenced by capillarity. This celebrated treatise has always appeared to me as the true successor of Gibbs's thermodynamical papers from which the chemist of to-day may still derive many suggestions. In it we find the sentence: "If the surface tension increases as a chemical action goes on, the capillarity will tend to stop the action, while, if the surface tension diminishes as an action goes on, the capillarity will tend to increase the action." Thomson attempted to prove this theoretical conclusion by experiments on the so-called "dead space." As is well known, alkali acts on chloral hydrate in aqueous solutions to yield chloroform, which separates throughout the solution as a white deposit of droplets except for a thin surface film where the solution is in contact with the air. This phenomenon was noticed first by Liebreich (*Z. physikal. Chem.*, 1890, 5, 529). Now Monkman showed that the surface tension increases while this reaction is proceeding. This might at first sight make an explanation of the "dead space" possible on the assumption that the formation of the chloroform is retarded in the surface, since surface tension increases. Yet, however satisfactory this explanation may appear, it is inadequate. The real explanation is probably much simpler. Budde (*ibid.*, 1891, 7, 586; *Wied. Ann.*, 1892, 46, 173) showed that the absence of chloroform droplets in the uppermost layer is probably merely the result of evaporation, the whole phenomenon being most sensitive to small differences in temperature. This earlier attempt to verify Thomson's theory was therefore not altogether successful.

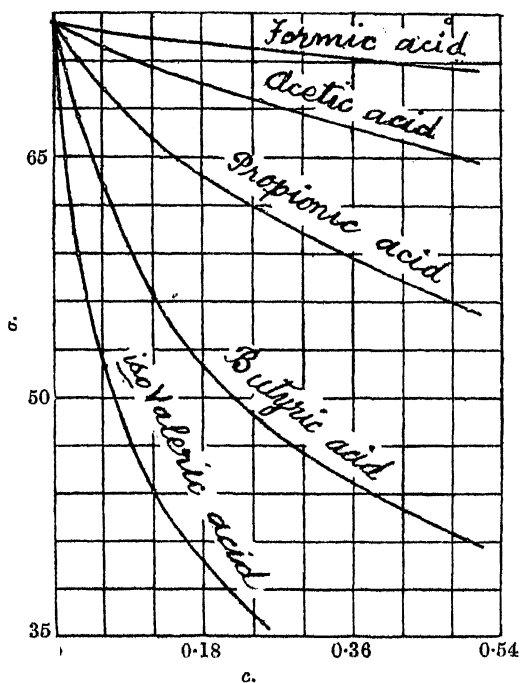
In the 40 years which have elapsed since then, a number of investigators have taken up this question. No case has been found simple and clear enough to afford a complete test of the theory;



the facts, however, agree with it on the whole. Before entering upon these investigations in detail, permit me to discuss some generalisations which I shall use.

Increase and decrease of surface tension caused by the dissolved substances are related to a change of concentration of these substances in the surface according to Gibbs's equation. If the surface tension increases or decreases with increasing concentration, the surface contains respectively less or more of the dissolved substance

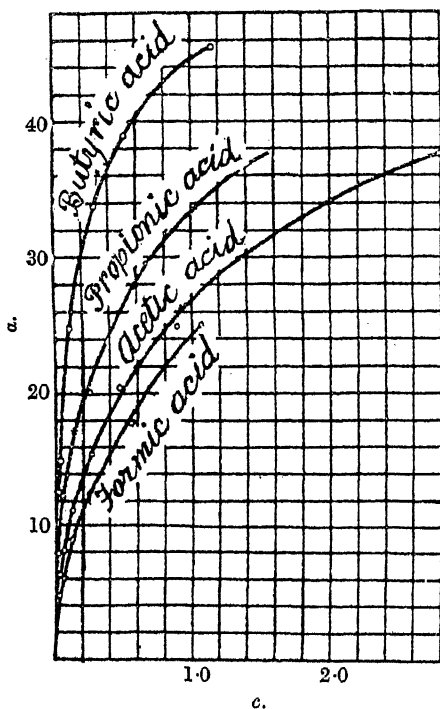
FIG. 1.



than the liquid in bulk. Let us call this change of concentration in the surface "adsorption." We then may assume that a substance is adsorbed negatively if it raises the surface tension, and is adsorbed positively if it lowers the surface tension. And Thomson's relation between capillarity and chemical equilibrium may be expressed in the following way: the displacement of chemical equilibrium in a surface takes place in a direction favouring those substances which lower the surface tension and are therefore adsorbed positively. Such substances are said to exert "capillary action," an expression which is perhaps not defined quite sharply.

It may be rather bold not to confine these speculations to liquid-gas or liquid-liquid surfaces, where we are really able to measure surface tension, but to extend them to surfaces of solid substances. Here we are not able to measure surface tension, at least not with any degree of precision, but we can easily enough find phenomena which may be considered as phenomena of adsorption. There is a great similarity in the behaviour of these different boundaries. Let me remind you of two facts. First, the so-called rule of Traube

FIG. 2.



holds good in aqueous solutions even if the second phase is a gas, a liquid such as mercury, or a solid such as charcoal. According to this rule, capillary activity increases strongly and regularly as we ascend any homologous series of organic substances. This becomes clear, for instance, in the decrease of surface tension in solutions of fatty acids as shown in Fig. 1, and in accordance with Gibbs's rule the adsorption increases as we rise in such a series. Figs. 2 and 3 show adsorption isotherms of fatty acids on charcoal and on siloxen ( $\text{Si}_6\text{O}_3\text{H}_6$ ), an enormously porous and strongly adsorbing substance prepared from

calcium silicide ( $\text{CaSi}_2$ ). The second fact is that organic (and many inorganic) acids and bases exhibit much greater capillary activity than their salts: they lower the surface tension more strongly and are accordingly adsorbed in a higher degree by most adsorbents. This may be explained by assuming that the ions are less active in this respect than the undissociated molecules.

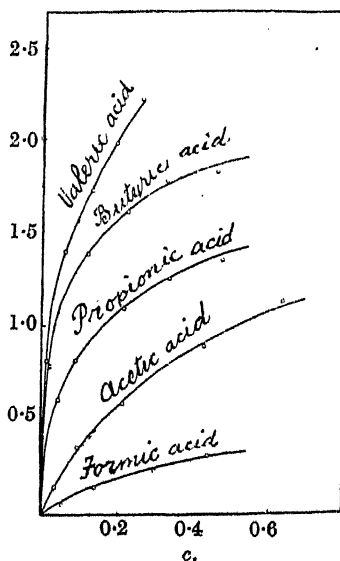
I am sure that surface chemistry will suffer many changes in the near future. But even if the ground on which we tread is not very firm, nevertheless I believe that we may generalise Thomson's relation and say that, on any surface, substances which are adsorbed

strongly are formed in large amount and the chemical equilibrium is therefore shifted in this direction.

Let me now return to the subject of my lecture. I shall commence by discussing a phenomenon which is rather complicated but has been known for a long time. If charcoal is shaken with salt solutions, especially those of salts with organic ions like dyes or alkaloids, the two ions are not always adsorbed in equivalent amounts; a dye kation, for instance, may be adsorbed more strongly than an inorganic anion, hydrogen ions replacing the lacking kations in the solution. This kind of exchange adsorption was perhaps considered to be of no great interest; it was assumed simply that some foreign substance (e.g., ash) in the charcoal exchanged some of its ions for ions from the solution. This explanation had to be given up, however, when Bartell and Miller (*J. Amer. Chem. Soc.*, 1922, 44, 1866; 1923, 45, 1106; Miller, *ibid.*, 1924, 46, 1150; 1925, 47, 1270) showed that a very pure charcoal made from sugar and containing less than 0.01% of ash behaved in a similar way: it adsorbed acids from salt solutions, the solution being alkaline after adsorption had taken place. The amount of acid calculated from the alkalinity of the solution agreed excellently with the amount found directly by washing the sugar charcoal with an organic solvent and titrating the acid. There was also a very distinct parallelism between the amount of acid adsorbed from the salt solution and the adsorbability of these acids in pure solution, for instance, for a benzoate, an oxalate, and a chloride. Here we really seem to have a hydrolysis of the salt caused by adsorption, a shifting of an equilibrium in such a direction that the production of the more strongly adsorbed substances—the acids—is favoured.

Recent investigations by Frumkin (Frumkin and Donde, *Ber.*, 1927, 60, 1816; Bruns and Frumkin, *Z. physikal. Chem.*, 1929, A, 141, 141; Burstein and Frumkin, *ibid.*, pp. 158, 219) have shown, however, that the conditions are more complicated and that the

FIG. 3.



electrical influence of the ions cannot be neglected. He activated an ash-free sugar charcoal in an electric furnace under a high vacuum up to  $1000^{\circ}$ , taking care that no air came in contact with the charcoal before it had adsorbed the dissolved substances. This charcoal did not appreciably adsorb weakly adsorbable inorganic substances such as hydrochloric acid or sodium hydroxide. If, however, the charcoal came in contact with air or oxygen it was able to adsorb acids such as hydrochloric acid but not alkalis. On the other hand, if the sugar charcoal was heated to  $1000^{\circ}$  in an atmosphere of hydrogen and carefully kept from the air, its behaviour was reversed : it adsorbed alkalis but not acids. Frumkin believes, therefore, that charcoal behaves like a gas electrode. If it contains oxygen, it gives off hydroxyl ions to the solution and takes up anions from it; the solution turns alkaline and loses an equivalent amount of anions. If the charcoal contains hydrogen, hydrogen ions are given off to the solution, kations are taken up from it, and it turns acid, losing an equivalent amount of kations. The adsorption of a weak and strongly adsorbable acid such as benzoic acid is not influenced by treating the sugar charcoal with hydrogen in the way described. In the case of the salts of weak acids, we may assume, therefore, that we really have a displacement of the equilibrium in the first sense, but especially for strong electrolytes the conditions are markedly modified by the presence of gases. In any case, we have no very well-defined case of the shifting of a chemical equilibrium by surface forces.

Experiments which leave no doubt as to the existence of such a displacement were recently made by Deutsch (*Ber.*, 1927, **60**, 1036; *Z. physikal. Chem.*, 1928, **136**, 353), in the Dahlem laboratory of the Kaiser Wilhelm Institut für physikalische Chemie. He found that indicators in solutions near their turning point changed their colour if the solution was shaken with an indifferent fluid such as benzene, toluene, etc. If, for instance, a solution of bromothymol-blue in a hydrogen-ion concentration of  $p_H$  7.4 is treated in this way, the colour changes from blue to yellow. This change of colour only takes place as long as fine drops of benzene are emulsified in the aqueous solution; it disappears as soon as the two phases have separated again. The more strongly the fluid is shaken, the more pronounced the colour becomes, because the droplets formed are finer and more numerous, their interface being accordingly larger. There can be no doubt that the colour change is caused by the emulsification, that is, by the formation of the large interface. The phenomenon is absolutely reversible, and may be repeated indefinitely. The colour changes as if the  $p_H$  had altered from 7.4 to 6.2. The shifting of the equilibrium between the different ions

and molecules characteristic for this indicator is of this order of magnitude.

This might be explained by assuming that the hydrogen-ion concentration in the surface of the droplets is different from that in the bulk of the liquid; but this does not hold, for if we take an indicator which is not an acid dye, such as malachite-green, it also changes on being shaken with an indifferent fluid. The change of the  $p_H$  which we would like to make responsible for the colour change has, however, a reversed sign in this case. With malachite-green the colour changes from yellow to green; this would correspond to a change of  $p_H$  from 0.5 to 1.5. Table I, as given by Deutsch, shows that acid and basic dyes seem to behave throughout in this way.

TABLE I.

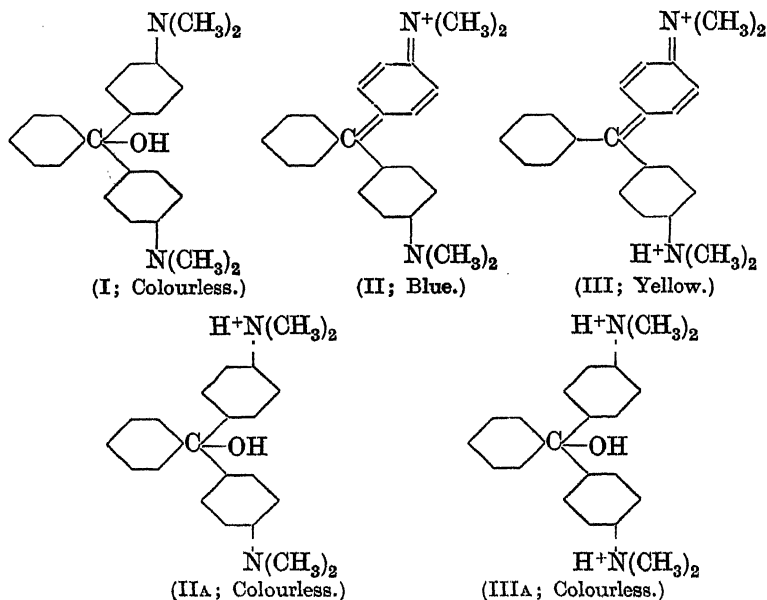
Indicator.	Solvent.	Colour of solution.	Colour on shaking.	Change of $p_H$ corresponding to colour change.
Guinea-green	About 1.0N-HCl	Yellow	Bluish-green	From 0.0 to 0.6
Malachite-green	„ 0.4 „	Yellow	Bluish-green	„ 0.5 „ 1.5
Brilliant-green	„ 0.25 „	Yellow	Greenish-blue	„ 0.7 „ 2.0
Methyl-violet	„ 0.1 „	Green	Blue	„ 1.0 „ 2.0
Thymol-blue	„ 0.016 „	Yellow	Reddish-violet	„ 2.8 „ 1.6
Tropæolin 00	„ 0.016 „	Orange-yellow	Red	„ 2.8 „ 1.8
Bromothymol-blue	Mixture of distilled and undistilled water.	Blue	Yellow	„ 7.4 „ 6.2

The change of interfacial tension agrees with Thomson's relation, as far as it has been tested hitherto, and in so far as it was sufficiently large to be tested. With malachite-green, for instance, the interfacial tension is lowered to 22% if the concentration of hydrochloric acid is changed from 0.43 to 0.25N, and the hydrogen-ion concentration ( $p_H$ ) alters correspondingly from about 0.5 to 0.7. This change causes a colour change similar to that which happens on shaking.

Before entering into the intricate question of determining what chemical changes are taking place in the interface, and how they are to be explained, I should like to point out that this phenomenon is found, not only at the interface of two liquids, but also at the surface of fluids in contact with a gas phase. It is not quite so easy to demonstrate it there, because the foam of the liquid has to be sufficiently stable to make the colour change visible. This is the case with thymolsulphonephthalein. If we shake a solution of this indicator having a  $p_H$  of about 2.8 with air or in a vacuum, where the

gas phase contains only water vapour, the foam turns reddish-violet, whereas the bulk of the liquid remains brownish-yellow.

It is no easy question to determine what chemical reactions are occurring in the interface. The reactions of these indicators are far from simple. There are generally quite a number of ions of different valency, a series of isomeric forms, and in many cases also amphoteric ions. Deutsch believes that the case of malachite-green permits us to draw certain conclusions. Under the conditions of the experiments, we have to consider 5 kinds of molecules (Rötger, Diss., Berlin, 1924) : 3 of a carbinol structure—an undissociated form and 2 ions—and 2 of a quinonoid structure—a univalent blue




kation and a bivalent yellow kation. It seems very likely that we have to deal only with the transformation of this yellow kation into the blue one. This would account for the colour change and for the fact that the reactions proceed quickly, whereas the conversions of the carbinol into the quinonoid forms go much more slowly. We have accordingly the change of a bivalent ion into a univalent one. This means that at the interface a less dissociated substance is formed. A similar conclusion may be drawn from the acid dye bromothymol-blue: the colour change at the interface agrees with the formation of a less dissociated molecule. Deutsch ventured to generalise these experiences and assumed that in all cases the formation of undissociated or less dissociated molecules is favoured in the

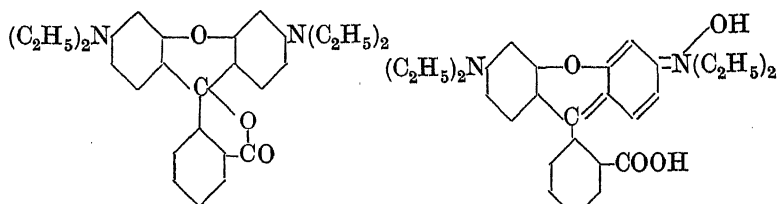
interface touching the gas phase or the phase of an organic liquid. This would agree with the general conception that the undissociated molecules are more strongly adsorbed than the ions by many adsorbents. I must confess, however, that Thiel (*Z. Elektrochem.*, 1929, 35, 266), for instance, who is a very good specialist in indicators, is not convinced that these colour changes found by Deutsch are always in accordance with the production of less dissociated molecules. He believes that in quite a number of cases, for instance with tropæolin and thymol-blue, the colour change at the interfaces is caused by the formation of other ions which need not be considered as less dissociated. In the case of tropæolin it is an amphoteric ion, and in that of thymol-blue most likely the ion of a carbonium base. We do not know enough about such ions to say whether their capillary activity is especially pronounced.

Rather surprising results were found by investigating the interface from the other side, so to speak. Deutsch dissolved the colourless base of rhodamine-0 in benzene and shook this solution with water. The emulsion formed turns deep red; in this case the phenomenon depends upon the droplets of water dispersed in the benzene. The colour disappears practically when the phases are separated again, the water in bulk being only weakly coloured from the red base of the dyestuff. This phenomenon is again markedly independent of the nature of the interface. If a piece of filter paper is dipped into the colourless solution of the base in benzene it turns red; this is also the case if dry quartz powder is used instead of filter paper.

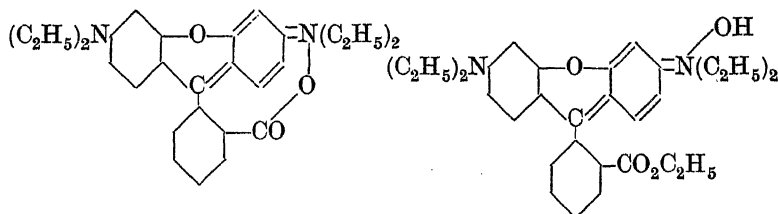
These experiments seem important in many respects. We see that a substance—in this case, the red base of the dye—may be formed at an interface, remaining very stable there, this substance being only formed in a very small amount or practically not at all when the area of the interface is too small. Further, it looks very much as if the change on the benzene side of the interface were a reversal of that on the aqueous side; that is, on the latter side, less dissociated substances seem to be favoured, these substances very often being such as would have dissolved in the organic liquid or in the gas phase (generally in the phase of the smaller dielectric constant) if such a solution were possible. On the benzene side, on the other hand, the same red substance, which is dissolved in the water, seems to be favoured. That this form is more dissociated than the colourless form in the benzene is most probable. We have to take into account the following possibilities. The colourless base is most likely a lactoid form. This is made plausible by the fact that some rhodamine dyes, which are esters, dissolve in benzene with a red or yellow colour and do not have a colourless base. Now the



constitution of these esters is such that conversion into the lactoid form is impossible. Therefore, this is most probably a colourless



Lactoid base.

*p*-Quinonoid ammonium base.

Betaine form.

Ester.

form of the base which is able to be formed by those dyes that are not esters. The red form of the base has most likely a quinonoid structure. We have two possibilities: an ammonium base of quinonoid structure, or the betaine form of the base. Some facts seem to indicate that we ought to prefer the latter. The ammonium base would need one more molecule of water than the betaine form. Now the presence of water does not seem absolutely necessary for the formation of the red base at an interface, for, if the benzene solution of the base is carefully dried with sodium, and if quartz powder, previously heated to redness and carefully protected from moisture, is added, the quartz turns red nevertheless. The change we are dealing with is therefore most likely the transition from the colourless lactoid form into the red betaine form. Now, according to the investigations of Bredig, Küster, and others, the betaine form has a great tendency to exist as an amphoteric ion. This is most likely the red substance with which we have to deal. The latter is to be considered as decidedly more dissociated, or at any rate as less saturated, than the lactoid form. The substance formed in the benzene side and soluble in water is therefore one which we may consider to be more dissociated.

Also, in the case of those rhodamine dyes like "rhodamine 6G extra" and "rhodamine 3G extra," which have the constitution of esters and dissolve in organic liquids in a coloured form, a change of colour takes place on shaking with water and on other interfaces. The bases of the two dyes mentioned are yellow in benzene solution,



and red in aqueous solution, in which they are much less soluble. When the benzene solution is shaken with water the colour turns red, and the same is the case if quartz is added to the benzene solution. The change is always in favour of the substance in the aqueous solution. This is perhaps in every case the amphoteric ion of the betaine form. In order that this substance be formed we must assume that the esters partly undergo a dissociation at the interface into the betaine form and alcohol.

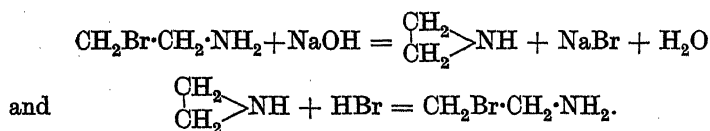
I should like to mention some more experiments which show in quite different cases how different interfaces may behave similarly. Fajans (Fajans and Hassel, *Z. Elektrochem.*, 1923, **29**, 495; Fajans and Wolff, *Z. anorg. Chem.*, 1924, **137**, 221) has investigated the adsorption of dyes on silver halides. Substances like silver eosinate suffer a distinct change of colour provided that the adsorbing surface of silver halides is covered with silver ions. This is the case if it is precipitated from a solution containing a surplus of silver ions. The colour changes from a pinkish-yellow with a green fluorescence to a distinct red on the surface of the halide. Now Deutsch and Fajans showed that the same colour change takes place at other interfaces. If a solution containing 0.01% of sodium cosinate and 0.01 mol. of silver nitrate (a solution which is pinkish-yellow with a green fluorescence) is shaken with benzene or pentane, a red precipitate is formed at the interface. The same happens if it is merely shaken with air. Instead of the silver salt a copper salt may also be used.

This may be explained in the following way. We start with a dilute solution of the eosinate of the heavy metal which is strongly dissociated and therefore shows the colour of the anion of the dye. On shaking, a large interface is formed, and the equilibrium is shifted in the direction of the undissociated salt, which, being less soluble, is precipitated. On the surface of the silver halide we also have the formation of the undissociated salt. This is why the colour change is the same at all interfaces. We are not able to decide whether this change of colour is caused by a deformation of the dye molecule, as Fajans believes, or whether an isomeric molecule (in the strict sense of the word) is formed.

Here we are already dealing with cases which are not strictly reversible and therefore do not belong rigidly to the scope of this lecture. Numerous irreversible reactions at interfaces are known in which insoluble substances are formed. I need only mention the acid soap on the surface of soap solutions (Laing, *Proc. Roy. Soc.*, 1925, *A*, **109**, 28) and the denaturation which proteins undergo if we shake their solution with air or other gases (Ramsden, *Z. physikal. Chem.*, 1904, **47**, 336).

Deutsch's experiments are valuable in that they show definitely that a displacement of chemical equilibrium at interfaces really exists and may be found in quite a number of cases. In some respects they leave much to be desired. It seems hardly possible to develop them in a quantitative form, since we are unable to assign a definite area to the interface. Furthermore, the chemical changes occurring are rather complicated. I therefore should like to discuss yet another case where precisely these points seem to be much simpler. Certainly there is another gap which cannot be filled in yet.

We may consider with certain restrictions that an equilibrium constant is equal to the ratio of the velocity coefficients of the forward and the reverse reaction. If we have a displacement of equilibrium at an interface, we may expect that the velocity of the one reaction will be increased, and that of the other diminished. A case of that kind was investigated by Juliusburger and myself. In homogeneous aqueous solutions we have the following two reactions:

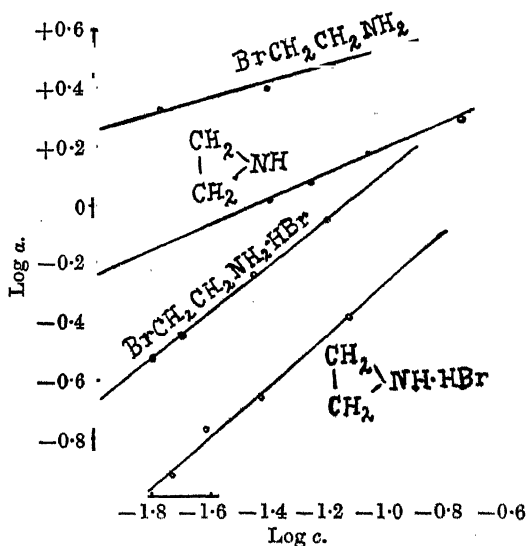


Bromoethylamine is unstable in alkaline solution and is transformed into the isomeric hydrobromide of dimethyleneimine, whereas in hydrobromic acid solution the hydrobromide of the latter is reconverted into bromoethylamine. [The formula of the substance formed in alkaline solution was the cause of some discussion. It was first considered to be the hydrobromide of vinylamine,  $\text{CH}_2\text{:CH}\cdot\text{NH}_2$ , but later investigations of Marckwald (Howard and Marckwald, *Ber.*, 1899, **32**, 2036; Marckwald, *Ber.*, 1900, **33**, 765; Marckwald and Frobenius, *Ber.*, 1901, **34**, 3544) showed that we have in any case to deal with an imine.] The velocity of the two reactions is easy to measure quantitatively: in the alkaline solution the amount of bromine ions increases—it is just doubled if, as is generally done, we start with the hydrobromide of bromoethylamine; and in the hydrobromic acid solution the amount of bromine ions diminishes. Now in acid solutions a secondary reaction goes on, the dimethyleneimine polymerising to a small extent; although this disturbance is not sufficiently marked to prevent us from measuring the velocity coefficients in acid solution, yet, since it is irreversible, it does not allow us to find the point of equilibrium in neutral solutions. Both reactions are well defined and are not affected by impurities. The transformation of the bromoethylamine is a reaction of the first order, and the reverse reaction is of the second

order, the velocity being proportional to the imine and bromine-ion concentrations.

Now these reaction velocities were measured in a heterogeneous system, the solutions being shaken with animal charcoal. It was necessary to know the adsorption of the following four substances: bromoethylamine, dimethyleneimine, and the hydrobromide of each. Fig. 4 shows, first, that the well-known adsorption isotherm agrees well with the measurements, for straight lines are obtained in a logarithmic plot. We see further that the bromoethylamine is adsorbed much more strongly than dimethyleneimine, and its

FIG. 4.



hydrobromide more strongly than that of dimethyleneimine. [Here we have a good example of salts being adsorbed much less than their bases.] According to the rule governing the displacement of chemical equilibrium at interfaces, we may expect that bromoethylamine, which has a stronger capillary activity, is more stable on the surface of the charcoal than in homogeneous solutions. The transformation of bromoethylamine into dimethyleneimine in alkaline solution ought therefore to be retarded, and the formation of bromoethylamine in acid solution to be accelerated. This is, indeed, the case, and in a very marked degree, as Figs. 5 and 6 show. We have first (Fig. 5) the velocity of the reaction in alkaline solution, the abscissæ indicating the time (in minutes), and the ordinates the percentage of bromoethylamine transformed; the reaction on the

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charcoal goes distinctly more slowly than in homogeneous solutions. In acid solutions (Fig. 6) the reaction on the charcoal is strongly accelerated. This latter reaction is disturbed, but only to a very small

Fig. 5.

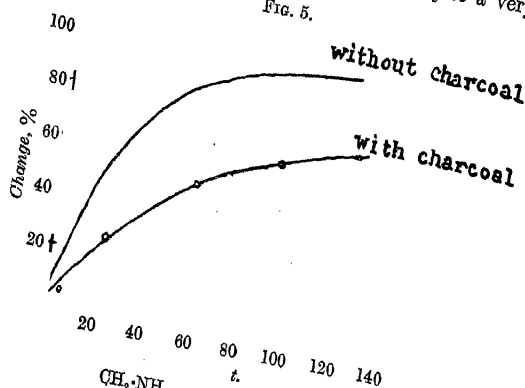
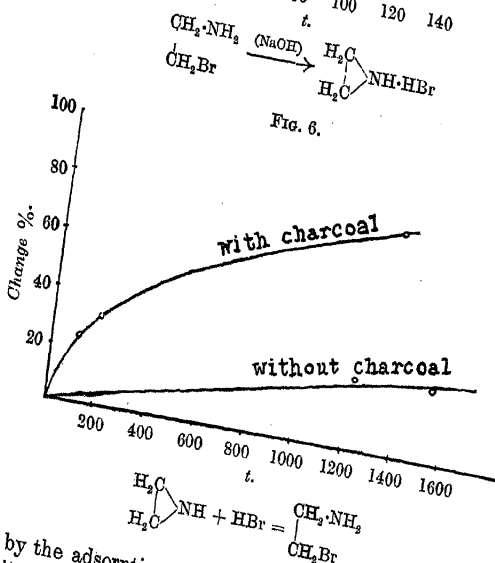


Fig. 6.



extent, by the adsorption of hydrobromic acid and some unknown change it undergoes at the surface of the charcoal. It is important to mention that under the conditions of these experiments the adsorption of the reacting substances was very strong, especially in the case of the alkaline solution. The amount of charcoal used was so large (several grams), and the concentration

of the reacting substances so low (generally  $N/20$  to  $N/50$ ), that the bromoethylamine was adsorbed to about 100%. We are really dealing with a reaction where the reacting substance is entirely in the adsorption layer. The conditions are therefore quite different from those prevailing in most catalytic gas reactions, in which only a small and generally unknown amount is adsorbed and reacts on the surface. In the reverse reaction the degree of adsorption is much lower; the hydrobromide of the dimethyleneimine is adsorbed at the commencement to about 15%.

It might have been objected to these experiments that we were not sure whether the reactions going on in the heterogeneous system are identical with those in the homogeneous system, but we were able to show that this is indeed the case. In alkaline solution the concentration of the bromine ion is doubled under both conditions, and in presence of charcoal the dimethyleneimine formed could be distilled off at temperatures below  $60^{\circ}$  (its boiling point is  $55^{\circ}$ ), and it formed its characteristic red crystalline salt with potassium bismuth iodide. It is not so easy to show that the reverse reaction is the same as in homogeneous solution, for we have no similar characteristic reagent for bromoethylamine. This, however, could also be shown in the following way: after the reaction had proceeded in acid solution in presence of charcoal, the solution was made alkaline, and the velocity measured with which dimethyleneimine was re-formed from the bromoethylamine originally produced in the acid solution. The reaction velocity coefficient thus measured was identical with that which had been found when bromoethylamine hydrobromide was used at the outset.

The mechanism of the two reactions in presence of charcoal is distinctly different, especially in one point, from that in homogeneous solutions. The reaction of the dimethyleneimine in acid solution is of the second order as in homogeneous solutions, the coefficient being much larger, however. On the other hand, the reaction of the bromoethylamine in alkaline solution does not follow the first order as it does in homogeneous solution. Since the reacting substance is, so to speak, totally in the adsorption layer, it is necessary to use as variable a surface concentration, *viz.*, the amount of amine divided by the amount of charcoal, and with this variable the velocity of the reaction is proportional to the  $\frac{3}{2}$  power of the surface concentration. We have not yet found an explanation for this empirical formula, but its discovery would probably provide the clue to a kinetic interpretation of this change of reaction velocity in presence of charcoal.

The behaviour in neutral solution presents some features of interest. As I said before, the equilibrium to be expected cannot be

measured exactly because of a secondary reaction which also disturbs the reaction in presence of charcoal; but it is quite clear that the formation of bromoethylamine is favoured strongly. For, starting with a neutral solution of bromoethylamine, about 90% is transformed in the course of a long time in homogeneous solution, whereas in presence of charcoal the reaction stops almost entirely when about 63% is transformed. If, on the other hand, we start with a neutral solution of the hydrobromide of dimethyleneimine, only about 10% is transformed in homogeneous solution, but more than 36% in presence of charcoal.

These experiments agree well with what we might expect from the theory: the equilibrium is displaced in the sense required by Thomson's relation, the formation of capillary active substances being favoured. The experiments show further that a substance, in this case the bromoethylamine, may be more stable at an interface than in homogeneous solution under similar conditions.

May I return once more to the question as to how far surface reactions are of biological importance? I need not emphasise the importance of microstructure and interfaces for protoplasma and life in general, since Professor Donnan did so most convincingly in his Liversidge lecture last year (J., 1929, 1387). Although life never means an equilibrium, but at most a stationary state like a flame or a water jet, a displacement of a chemical equilibrium may make itself felt in the change of reaction velocities, as in our case of the transformation of bromoethylamine into dimethyleneimine. We may therefore assume that the formation of capillary active and strongly adsorbable substances is favoured generally if the aqueous phase which certainly constitutes some part of a protoplasmic entity comes into contact with a solid or a liquid organic substance of small dielectric constant. Many substances of biological importance, indeed, exhibit capillary activity, *e.g.*, the alkaloids and fats.

The fact that at interfaces substances may be formed, and even possess considerable stability, whereas at the same concentrations without the interfaces their existence is transitory, may account for the extraordinary structure of many substances playing important biological rôles. I have always been astonished at the great difference between the organic chemistry of our laboratories and that under biological conditions. Not only is the difference in the methods used remarkable—in laboratories we use a large range of temperatures and a great variety of solvents, whereas Nature utilises a small range of temperatures and a great variety of interfaces—but the substances formed also seem to me to be very different. I doubt whether an organic chemist, knowing nothing about natural products

but, on the other hand, well trained in all methods of work and master of all our knowledge of the possibilities of chemical valency and even more, I doubt whether he could have conceived the existence of substances like most alkaloids or cholesterol, lecithin, adrenaline, thyroxine, and many others. This may be caused partly by the fact that we know a good deal of what happens in the bulk of solutions, but very little about what takes place at interfaces. And I mean not only comparatively inert interfaces, such as air or charcoal, but also those which are very reactive. We must realise that we have to deal, not only with the relatively simple displacements discussed in this lecture, but also with a great number of further reactions which may take place if the unstable substances stabilised at an interface react with other substances at the interface or with the molecules of the adsorbent itself. I should not be surprised if the great difficulty which we meet in trying to explain the nature of enzymes is partly due to similar causes. They may be very unstable and active organic substances, perhaps even organic radicals which are stabilised because they are adsorbed at a suitable interface, but they are able to react very energetically in intermediate reactions with other substances also adsorbed on these interfaces.

## NOTES.

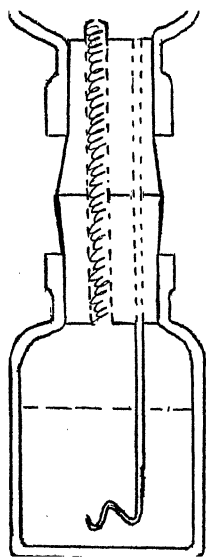
*An Apparatus for the Determination of Solubility.* By

ALAN N. CAMPBELL.

IN some very accurate work on the physical properties of optical antipodes (*Nature*, 1929, **124**, 792), it became necessary to determine solubilities with great accuracy, and any such method as the removal of samples from a bottle in the thermostat by means of a warmed pipette was obviously out of the question. Previous work with Goldschmidt's apparatus (*Z. physikal. Chem.*, 1895, **17**, 153) had shown that, although this embodies the important principle of filtering in the thermostat, it had certain objections: (1) it is too cumbrous; (2) suction is employed, whereby, if the solid is fine or slimy, it becomes clogged in the filter-plug and the apparatus has to be cleaned out. Accordingly the apparatus shown in the diagram was designed. It possesses the advantages of compactness and simplicity, for when it is inverted in the thermostat, filtration takes place.

The bottles are of the ordinary wide-mouthed 1-oz. type, except that the mouth of the top one is ground. Glass tubes pass through the bungs as shown. The wider tube (of 3 mm. internal diameter)

is constricted at the top and packed with glass wool. The other (quill) tube is drawn out to a capillary and bent into an S. As the liquid entering this tube at the beginning is pure solvent, which would dilute the saturated solution when subsequently expelled by the air pressure from below, it is advisable to arrange that all the immersed tube is of capillary diameter. The very small amount of pure solvent then expelled (perhaps 0.1 c.c.) is negligible in comparison with the total volume, especially when it is remembered that the whole solution then passes slowly through a layer of the solid.



× One-half.

The lower bottle is charged with solid and solvent and the apparatus fixed in a vertical position on the horizontal paddle of the thermostat stirrer. When dissolution is complete, the apparatus is inverted in the thermostat, and the solution filters through the plug, air being displaced into the upper chamber through the narrow tube. The double bend at the mouth of the latter prevents the entrance of solid matter into the lower bottle. The apparatus is then removed from the thermostat and the appropriate (weighed) bottle closed with a ground-glass plate.

The apparatus works perfectly, and should be very suitable for phase-rule studies, involving the analysis of the wet solid phase. The slight increase of gas pressure in the apparatus at the temperature of the thermostat prevents the leaking in of thermostat water. At high temperatures the apparatus should be enclosed in a grip to prevent the increased pressure forcing out the bungs.—UNIVERSITY OF ABERDEEN. [*Received, December 9th, 1929.*]

*2'-Nitro-2- and -4-aminodiphenyl Sulphides and 4'-Nitro-2- and -4-aminodiphenyl Sulphides.* By HERBERT HENRY HODGSON and WOLF ROSENBERG.

THE requisite diaminodiphenyl sulphide (25 g.) was dissolved in alcohol (200 c.c.), and sodium wire (5 g.) added at a rate sufficient to maintain regular ebullition (under reflux); after boiling for one hour, the mixture was treated with *o*- or *p*-chloronitrobenzene in slight excess of the amount required for the condensation



$\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SNa} + \text{C}_6\text{H}_4\text{Cl} \cdot \text{NO}_2 \longrightarrow \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 + \text{NaCl}$ , then boiled 2 hours longer and filtered hot. Only 4'-nitro-4-amino-diphenyl sulphide crystallised from solution on cooling; in the other cases alcohol, unchanged chloronitrobenzene, and any chloroaniline formed as by-product were removed by steam distillations and the tarry residue was crystallised three times from alcohol (charcoal). Constitutions were confirmed by reduction to the known diamino-diphenyl sulphides.

	M. p. and % S ( $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_2\text{S}$ requires S, 13%).	Colour of alcoholic solution.	Colour change of alcoholic solution with		Dry product with conc. sulphuric acid.
			chlorine water.	bleaching powder.	
Diphenyl sulphide.					
2'-Nitro-2-amino- (bright yellow plates)	81.5°; 13.2	Greenish- yellow	Brown with light sal- mon flocks	Pale brown	Yellow
2'-Nitro-4-amino- (golden-brown plates)	102°; 13.2	Brown- yellow	Light brown with brown flocks	Pale brown	Deep red changing to blue and violet on heating
4'-Nitro-2-amino- (brown-yellow prisms)	98°; 12.0	Greenish- yellow	Pale brown with sal- mon-pink flocks	Pale brown	Orange
4'-Nitro-4-amino- (bright orange-yellow leaflets)	143°; 13.2	Greenish- yellow	Light brown with yel- low flocks	Pale brown	Red-orange
	(compare Kehrman and Bauer, <i>Ber.</i> , 1896, 29, 2362)				
2:4'-Diamino- (colourless prisms from dilute alcohol)	62.5°; 15.0 (Calc. 14.8)	(compare Nietzki and Bothof, <i>Ber.</i> , 1894, 27, 3261; 1896, 29, 2774)			

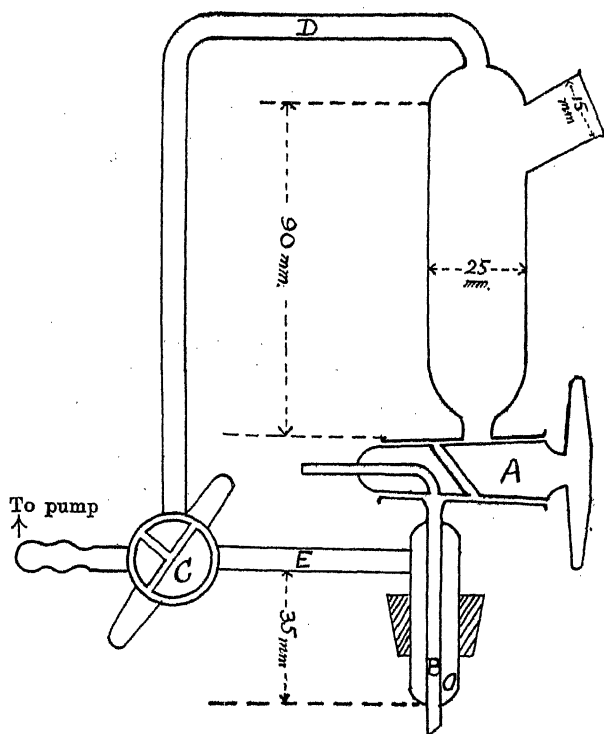
The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals.—TECHNICAL COLLEGE, HUDDERSFIELD.  
[Received, November 13th, 1929.]

*The Solubility of Sodium Thiocyanate in Alcohol.* By JAMES  
RIDDICK PARTINGTON.

IN a recent communication (Hughes and Mead, J., 1929, 2282) the authors state that, for the solubility of sodium thiocyanate in alcohol, "no data are at present available." This statement is incorrect, since Dr. F. E. King and I published a series of experiments on this subject some little time ago (*Trans. Faraday Soc.*, 1927, 23, 522). The method of preparation of the salt was the same as that described by Hughes and Mead; their value for the solubility at 25° is, however, somewhat lower than ours, which may be due to the fact that the salt used by them was somewhat purer than ours, or, equally possibly, to some other cause. It may be mentioned that several experiments on the solubilities of salts in non-aqueous solvents have been published from this laboratory, and that several more are in progress.—EAST LONDON COLLEGE, UNIVERSITY OF LONDON.  
[Received, November 29th, 1929.]

*An Improved Receiver for Vacuum Distillation.* By GEORGE  
ARMAND ROBERT KON.

THE accompanying figure illustrates a form of receiver for vacuum distillation which has been in use in these laboratories for some time. It is simpler and cheaper than the ordinary "Perkin triangle," as it has only two taps instead of three; another advantage is that when air is admitted through the tap *A* to the lower portion of the appar-



atus in order that the receiving flask may be changed, the last few drops of distillate remaining in the tube *B* are blown into the receiving vessel, thus minimising waste. The three-way tap *C* enables connexion to be made between the pump and either or both halves of the apparatus. It is, of course, possible to construct the apparatus with two rubber joints at *D* and *E* to allow receivers of different sizes to be used, but the all-glass apparatus illustrated is preferable, and as it is very compact, breakages are rare.\*—IMPERIAL COLLEGE OF

\* The apparatus described can be obtained from Messrs. Howard Rawson & Co., Pond Place, Fulham Road, London, S.W. 3.

SCIENCE AND TECHNOLOGY, SOUTH KENSINGTON, S.W. 7. [Received, December 11th, 1929.]

*Preparation of 4- and 6-Hydroxy-3-nitrophenylarsinic Acids.*

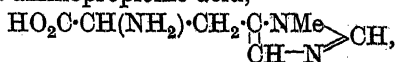
By ISIDORE ELKANAH BALABAN.

CLAUS and STIEBEL (*Ber.*, 1887, **20**, 1379) reduced 2:4-dinitrochlorobenzene and obtained a mixture of 4- and 6-chloro-3-nitroaniline consisting almost wholly of the 6-chloro-compound: no yields are stated. These bases can be readily obtained by West's method (*J.*, 1925, **127**, 494), the yields being 23.0% and 45.0% of 4- and 6-chloro-3-nitroaniline respectively.

When the bases are submitted to the Bart-Schmidt reaction, 4-chloro-3-nitrophenylarsinic acid (yield, 32.4%) and 6-chloro-3-nitrophenylarsinic acid (yield, 32.9%) are obtained (compare Balaban, *J.*, 1928, 809); and when these acids are boiled under reflux with 25% aqueous sodium hydroxide (10 c.c. for each gram) for 3 hours, they are converted into 4-hydroxy-3-nitrophenylarsinic acid (yield, 45.6%) and 6-hydroxy-3-nitrophenylarsinic acid (yield, 73.0%).—RESEARCH LABORATORY, MESSRS. MAY & BAKER LTD., WANDSWORTH, S.W. 18. [Received, December 7th, 1929.]

*Anserine.* By FRANK LEE PYMAN.

LINNEWEH, KEIL, and HOPPE-SEYLER (*Z. physiol. Chem.*, 1929, **183**, 11) have recently shown that anserine yields on hydrolysis  $\beta$ -aminopropionic acid and an *N*-methyl derivative of *dl*-histidine. On distillation with soda-lime, anserine gave a dimethylglyoxaline which they identified with the dimethylglyoxaline obtained by Jowett (*J.*, 1903, **83**, 438) by distilling *isopilocarpine* with soda-lime, since it gave a chloraurate, m. p. 220—225°, Jowett giving m. p. 214—215°. They have overlooked the fact that the constitutions of the 1:4- and 1:5-dimethylglyoxalines have since been determined (Pyman, *J.*, 1910, **97**, 1814; 1922, **121**, 2616; Burtles, Pyman, and Roylance, *J.*, 1925, **127**, 581), and that it has been shown that the chloraurates melt at 137—138° and 218—219° respectively. Their dimethylglyoxaline is thus 1:5-dimethylglyoxaline and consequently their methylhistidine is *dl*- $\beta$ -(1-methylglyoxalanyl-5)- $\alpha$ -aminopropionic acid,



and not the 1:4-isomeride formulated in their paper. The relative positions of the side chains and the *N*-methyl groups are thus the

same in anserine and pilocarpine.—RESEARCH LABORATORIES, MESSRS. BOOTS PURE DRUG CO. LTD., NOTTINGHAM. [Received, December 18th, 1929.]

*The Mechanism of Cyanoacetamide and Cyanoacetic Ester Condensations.* By CHRISTOPHER KELK INGOLD.

BARDHAN'S account (J., 1929, 2233) of the author's views on the condensation of ethyl cyanoacetate and similar substances with keto-enolic compounds requires adjustment. The only reference given by Bardhan in this connexion is to a paper (1921) by the author in which the conclusion was drawn that, since tendency to enolisation bears a close relation to tendency to condensation, the latter reaction involves the enol. Kohler and Corson's later demonstration (1923) that, notwithstanding the experience of previous observers (Thorpe, 1905; Haworth, 1908), condensation is possible with a ketone incapable of enolisation was naturally accepted by the author as proving that his former view was inadequate as a general conception, and in 1926, with Cooper and E. H. Ingold, he again discussed the Michael and aldol reactions in terms the application of which to cases of the type considered by Bardhan is that the cyanoacetamide or ethyl cyanoacetate anion may unite with the acetylacetone analogue either at  $C_\alpha$  (electron-displacements  $\alpha$ ; aldol reaction) or at  $C_\gamma$  (displacements  $M$ ; Michael reaction),

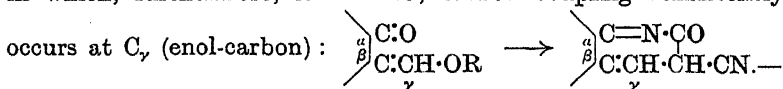
$\text{HO}-\overset{\overset{M}{\curvearrowright}}{\underset{(\gamma)}{\text{C}}}=\overset{\overset{\alpha}{\curvearrowright}}{\underset{(\alpha)}{\text{C}}}-\text{O}$ , and that a similar statement should apply to

ketones generally, unless the second alternative disappears because the unsaturated system is insufficiently extended to admit of displacements  $M$ . It is also part of the theory that tendency to condensation (aldol reaction; or Michael reaction, if constitutionally

possible) and tendency to enolisation,  $\text{H}-\overset{\overset{\alpha}{\curvearrowright}}{\text{C}}=\overset{\overset{\beta}{\curvearrowright}}{\text{C}}-\text{O}$  (if constitutionally possible), are different manifestations of the same electron-attraction of carbonyl oxygen—which is why the two phenomena are related. The omission by Bardhan of any reference to this and subsequent cognate papers, together with his consistent use of the present tense in ascription to the author of the older views which these papers modify and supersede, are misleading features in his account.

With regard to the decision between  $C_\alpha$ - and  $C_\gamma$ -carbon-coupling (where both possibilities are open, as in enolising 1:3-dicarbonyl compounds), a method of envisaging such problems has been advanced by Burton and the author (1928), and a mass of consistent

empirical observation is available. It is therefore surprising that Bardhan, whose own observations on the reaction between cyanoacetamide and enolising 1 : 3-dicarbonyl compounds are indecisive in the absence of knowledge of the direction of enolisation, nevertheless contends that carbon coupling at  $C_\alpha$  (carbonyl carbon) is the general mode of reaction in this and allied condensations. No reference is made to the large body of significant contrary indications—even to such as directly relate to the particular reaction studied, as, for instance, the observations of Errera (1900), Simonsen (1908), and Sen-Gupta (1915) that in the condensation of cyanoacetamide with hydroxymethylene-ketones, in which the direction of enolisation is beyond doubt, and with ethoxymethylene-ketones, in which, furthermore, it is fixed, carbon coupling consistently



THE UNIVERSITY, LEEDS. [Received, November 6th, 1929.]

## XXV.—*The Influence of Hydrogen and of Water Vapour on the Ignition of Carbon Monoxide.*

By ARTHUR SMITHELLS, HENRY WHITAKER, and THEODORA HOLMES.

### *Introduction.*

THE experimental work now recorded was commenced some years ago at the University of Leeds by Mr. H. Whitaker, and the point at issue seemed to be determined satisfactorily by 1923. Subsequently, however, further verification was deemed desirable before publication. Professor H. B. Baker advised the continuation of the work and, thanks to his kindness and to the generosity of the Worshipful Company of Salters in providing assistance, the experiments were resumed after a long interval by Miss Holmes. The greater part of the designing of the apparatus and the whole of the actual execution of the work fell to Mr. Whitaker and Miss Holmes, and in the second stage we have had the great advantage of being able always to count upon Professor Baker for advice.

The experiments arose from some rather speculative deductions (which I no longer entertain) from the Lewis-Langmuir cubical atom conceptions soon after they appeared. In attempting to apply them to the standing problem of the combustion of carbon monoxide, I found they appeared to give a plausible explanation of a striking observation made shortly before by Bone and Haward

(*Proc. Roy. Soc.*, 1921, *A*, **100**, 67). In their experimental study of gaseous combustion at high pressures, they had obtained results which showed a "peculiar influence of hydrogen in accelerating the rise of pressure in the explosion of hydrogen-carbon monoxide mixtures at high pressures, an effect which can be shown to be altogether disproportionate to the volumetric amount of it present." They add: "Our experiments seem to point to hydrogen being even more potent than its equivalent of steam as a promoter of the combustion of carbonic oxide (though this is a matter needing further investigation)." It appeared desirable to try to measure the relative catalytic influence of hydrogen and water vapour on the initial ignitability of a carbon monoxide-oxygen mixture in a eudiometer at or near atmospheric pressure.

Since 1921, the relative catalytic influence of water and steam on the combustion of carbon monoxide has acquired greater interest and has been the subject of much investigation. Professor Bone and his collaborators have followed up the original experiments and made many new ones of an exact quantitative character bearing on the subject during their researches on the combustion of gases at high pressure. Bone, Newitt, and Townend (*J.*, 1923, **123**, 2008) obtained definite evidence that the substitution of hydrogen for a small part of the carbon monoxide had a specific accelerating effect on the rising pressure curve much greater than that produced by an addition of water vapour. Later, the same authors (*Proc. Roy. Soc.*, 1928, *A*, **120**, 546) and Bone, Townend, and Smith (*ibid.*, p. 563) recorded further experiments on the relative influence of hydrogen and steam on the carbon monoxide combustion. These cannot be summarised without quoting numerical values, but they confirm and amplify Bone's earlier conclusions in reference to the relative influence of hydrogen and water vapour as catalysts. An important matter in the last-named paper is the reference to "the sensitiveness as regards explosion time of theoretical carbon monoxide-air explosions to slight changes in hygroscopic conditions at high initial pressures, even though the moisture actually present in the system be less than 0.04 per cent."

Other relevant observations are those of Dixon and Walls (*J.*, 1923, **123**, 1025), who found that the carbon monoxide-oxygen mixture with 5.5% of water vapour had a maximum rate of explosion of 1738 m./sec., whereas with 5.5% of hydrogen the rate was 1782 m./sec.

Payman and Wheeler (*ibid.*, p. 1251) concluded that "whereas a trace of water vapour is more effective in enabling propagation of flame to take place in dried mixtures of carbon monoxide and air, twice as much of it is required to give to that propagation its com-

plete freedom." They found that the amounts necessary for this were 6% of water and 3% of hydrogen.

Fenning (*Phil. Trans.*, 1926, *A*, 225, 331), in a study of carbon monoxide-air explosions in a closed vessel, found that with hydrogen less time was taken to reach maximum pressure than with water vapour.\*

An excellent account of investigations relating to the combustion of carbon monoxide, beginning with Dixon's primary discovery of the influence of water, is given by Bone and Townend ("Flame and Combustion in Gases," Longmans, 1927).

(A. S.)

The present experiments aimed at a direct comparison of the efficiency of hydrogen and water vapour in facilitating the ignition of a mixture of carbon monoxide and oxygen by passing a spark through two eudiometers in series, one containing, beside the carbon monoxide and requisite oxygen, a known amount of hydrogen, and the other an equimolecular amount of water vapour.

*Preparation and Purification of Gases.*—The carbon monoxide was prepared in an apparatus similar to that used by Waran (*Phil. Mag.*, 1921, 42, 246) by adding redistilled formic acid to pure sulphuric acid. The gas was passed through (1) potassium hydroxide solution to remove any carbon dioxide, (2) sulphuric acid to catch any alkaline spray and act as a preliminary drying agent, (3) phosphoric oxide tubes for final drying, and (4) a tube cooled by liquid air.

The oxygen, prepared by heating potassium permanganate, passed through (1) a tube containing solid potassium hydroxide and glass wool, (2) phosphoric oxide tubes, and (3) a liquid-air tube.

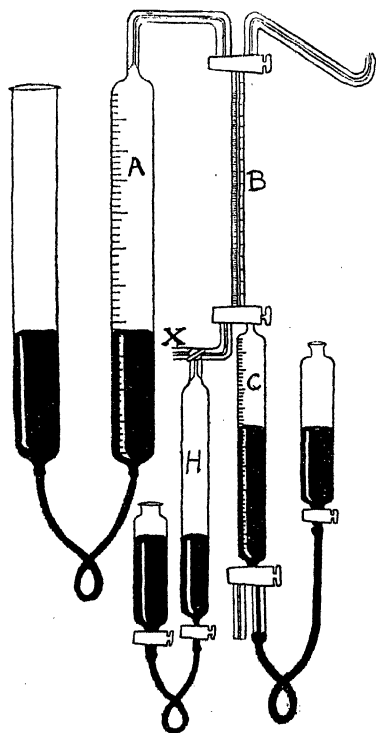
The hydrogen was prepared by electrolysis (see Baker, J., 1902, 81, 7, 400) between platinum electrodes, of baryta, recrystallised three or four times, dissolved in conductivity water. It was passed through (1) an electrically heated tube containing copper gauze, which had previously been heated to redness first in a current of dry air and finally in a current of dry hydrogen, to remove any oxygen which might have diffused into the hydrogen during electrolysis; (2) a liquid-air tube; (3) a calcium chloride tube for preliminary drying; and (4) phosphoric oxide for final drying.

*Water Vapour.*—To obtain an admixture of water vapour in desired proportion with the combustible gases, dilute sulphuric

\* The paper just published by Garner and Roffey (J., 1929, 1123) on "The Effect of the Addition of Hydrogen and Water on the Radiation emitted from the Carbon Monoxide Flame" is of great interest in relation to our own experiments.

acid was used, 1 c.c. of the liquid being passed into the eudiometer by means of a bent pipette, and the temperature at which the tube must be kept to maintain the required vapour pressure was calculated. The vapour-pressure values used were taken from Regnault's tables; although doubt has been thrown upon his values at such high concentrations, it is believed that they are not so inaccurate as to invalidate the conclusions drawn from these

FIG. 1.



150 c.c., (B) 2 c.c., (C) 12 c.c., and a fourth tube (H) of approximately 100 c.c. capacity. The apparatus was cleaned with chromic acid mixture, washed with distilled water, steamed out for some hours, and dried by the passage of hot dry air, the apparatus itself being heated wherever possible.

After calibration of the graduated tubes, the apparatus was dried finally and filled with freshly distilled mercury. The carbon monoxide and oxygen were mixed in the required proportion in the large tube A by connecting the apparatus at X successively to the two generating apparatus. From this mixture the required

experiments. Careful tests showed no measurable evolution of gas from the contact of the diluted acid with mercury under all the conditions of the experiments.

*Phosphoric Oxide.*—The phosphoric oxide used was prepared by redistillation in a current of oxygen, and was shown to be of a high degree of purity. For some of the earlier experiments, highly purified material kindly supplied by Sir Richard Threlfall, F.R.S., was used.

*Ignition Arrangements.*—The gas mixture was subjected to a spark from the secondary of an induction coil run at a constant voltage.

*Gas Storage and Dilution Apparatus.*—The gases were collected and mixed in the proportion of 2 vols. of carbon monoxide to 1 vol. of oxygen in the apparatus shown in Fig. 1. This consisted of three graduated tubes of approximate capacities (A)



volume for an experiment was withdrawn into the graduated tube C, where it was exactly measured, before being passed through B and the delivery tube into the eudiometer.

As accurately known, very small volumes of hydrogen were required in the experiments, this gas was first mixed in measured proportion with a large volume of carbon monoxide-oxygen mixture and then added in small quantities to the main bulk of the two gases used in an experiment. This was carried out by filling the narrow-bore tube B with pure hydrogen and passing any desired volume of it into the carbon monoxide-oxygen mixture in A. After allowing time for complete admixture, the diluted hydrogen was passed into H for storage.

*Explosion Tubes.*—The experiments were carried out in glass eudiometers of approximately 1.5 cm. internal diameter with platinum wire electrodes. The gap between the electrodes was fixed and measured under a travelling microscope.

The eudiometers were cleaned as previously described, and carefully dried by the passage of purified, dry air while the ends were heated strongly.

To remove occluded gas in the electrodes, sparks were passed across them for some hours while a current of pure, dry oxygen was passed through the eudiometers. They were then filled with freshly distilled mercury, which was immediately replaced by a known volume of the gas mixture from the storage apparatus.

As the eudiometers had to be water-jacketed during an experiment, it was necessary to insulate the junctions of the electrodes with the leads. This was done in the earlier experiments by fitting vertical glass tubes with their ends bent suitably to cover the projecting loops of the electrodes, the junction being held and covered by a ring of rubber tube. These vertical tubes were filled with mercury and the leads dipped into their open ends. In the later experiments, the projecting ends of the electrodes were protected with enamel beads to which rubber tubes were attached as shown in Fig. 2. By attachment of a second limb of tubing, as a levelling tube, to the mouth of the eudiometer, and adjustment of the mercury column in it, atmospheric pressure was secured in the gas mixture. The ends of the levelling tubes were closed with rubber caps during the sparking to prevent scattering of the mercury.

*Temperature Control.*—The arrangements for temperature control are shown in Fig. 3. The eudiometers were fixed in inverted bell-jars which served as water-jackets, and water flowed into these continuously from a thermostat reservoir.

*Procedure.*—In each experiment one eudiometer, containing only carbon monoxide and oxygen in combining proportion and phos-

phoric oxide, was used as a control. Immediately upon charging the first eudiometer a second was taken, and to it was added the gas mixture containing a known small quantity of hydrogen. A small stick of compressed phosphoric oxide was passed up this tube and floated on the mercury surface. (The volume of the stick was about 1 c.c., and the entangled air not more than 0.1% of the total volume of gas in the eudiometer.) In a third eudiometer containing the carbon monoxide-oxygen mixture, 1 c.c. of suitably diluted sulphuric acid was brought on to the mercury surface by means of a bent pipette. The eudiometers so arranged were allowed to stand for at least 10 days, and if a spark then failed to fire the mixture in the control eudiometer, the experiment was

FIG. 2.

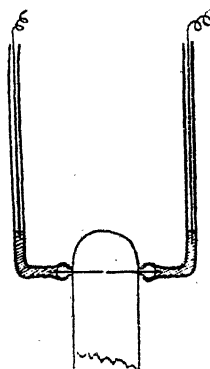
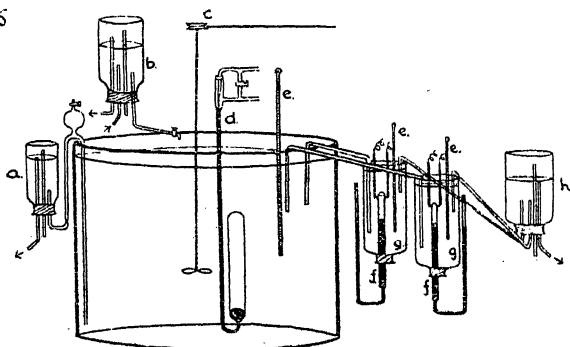


FIG. 3.



- |                       |                             |
|-----------------------|-----------------------------|
| a. Water leveller.    | c, e, e. Thermometers.      |
| b. Water inlet.       | f, f. Eudiometers.          |
| c. Stirrer.           | g, g. Inverted bell-jars.   |
| d. Thermal regulator. | h. Bell-jar water leveller. |

proceeded with. The water-jackets of the two other eudiometers were connected with the thermostat reservoir and kept at a temperature sufficient to give in the third eudiometer a concentration of water vapour molecularly equal to that of the hydrogen in the second eudiometer. After 3 days had been allowed for the attainment of liquid-vapour equilibrium, the electrodes of the two eudiometers were connected in series to the coil and a single spark was passed. If this failed to produce ignition in either tube, sparking was continued for some seconds.

### Results.

The results of the first two series of experiments are in Tables I and II, those in Table I, which were made at Leeds, being merely preliminary. It was, of course, sought in each experiment to have

equal volumes of the carbon monoxide-oxygen mixture for trial with equal hydrogen and water additions. The exact measurements of these volumes with hydrogen and water vapour respectively in each experiment show such a close approach to equality that, to avoid complicating the table, a mean figure is used.

TABLE I.

	Volume of gas, c.c.	Hydrogen, %.	Conc. and temp. of $H_2SO_4$ soln. required to give volumes of water vapour equivalent to hydrogen.	Time of drying, days.	Behaviour on sparking.	
					Water mixture.	Hydrogen mixture.
1.	10.04	3.4	0.0%; 22.2°	13	Instant flash	Instant flash
2.	10.09	0.48	60%; 20.2	23	Instant flash	Instant flash
3.	9.26	0.044	84.5%; 34.5	16	Flame travelled slowly	Blue flash
4.	9.89	0.037	84.5%; 30.7	14	No ignition	Flash
5.	12.64	0.037	84.5%; 28.0	15	No ignition	Flash
6.	9.96	0.042	84.5%; 29.4	18	No ignition	Blue flash

TABLE II.

1.	7.45	0.049	82.4%; 25.8°	38	No ignition	Ignition
2.	8.70	0.049	81.7%; 25.0	24½	"	"
3.	6.65	0.048	81.7%; 23.75	20	"	"
4.	7.43	0.047	82.4%; 24.9	126	"	"
5.	8.10	0.045	80.5%; 36.2	126	"	"
6.	7.25	0.045	80.5%; 26.0	105	"	"
7.	4.80	0.057	80.5%; 30.0	15		
8.	5.50	0.058	80.5%; 30.2	10		
9.	7.45	0.032	81.7%; 20.0	23		No ignition

Table I indicates that below approximately 0.04% of catalyst there is a difference in the effects of hydrogen and water vapour. From Table II, it is seen that with proportions of both hydrogen and water vapour throughout the range of about 0.03 to 0.06% the hydrogen alone conferred ignitability, except in Expt. 9, where there was no ignition in either tube. This value is slightly higher than that found in the preliminary experiments. The difference may well be due to the different sparking conditions, for a different sparking coil was used. Also, in the earlier experiments (Table I) the pressure was only approximately atmospheric and varied slightly in the two tubes.

*Minimum Proportions of Hydrogen and Water Vapour required to permit Spark Ignition.*—It will be seen in Expt. 9 of Table II that, when the concentration of hydrogen had been reduced to 0.032%, the mixture no longer ignited. This observation was verified, and an attempt was made to ascertain the limit more closely by beginning with a mixture containing approximately 0.02% of hydrogen and adding further small quantities of hydrogen.

Table III gives the results, from which it appears that the 0.032% of Expt. 9 was in fact about the limiting concentration.

TABLE III.

Volume, c.c.	Hydrogen, %.		Temp.	Press., mm.	Time of drying.
	No ignition.	Ignition.			
7.2	0.023	0.033	18°	760	18 days
7.2	0.021	0.041	18	760	18 „
9.4	0.032	0.049	25	762	23 „
7.3	0.018	0.032	17	760	19 „
4.63	0.018	0.038	19	768	3 months

An attempt was also made to discover the limiting concentration of water vapour that determined ignitability. This was done by a step-wise elevation of the temperature of a submerged eudiometer containing the gas mixture and diluted sulphuric acid. The results given in Table IV show that the limiting concentration is approximately 0.12% of water vapour.

TABLE IV.

Volume of gas, c.c.	Conc. of H <sub>2</sub> SO <sub>4</sub> , %.	Time, days.	Press., mm.	Temp. between which igni- tion occurred.	Equivalent percentage of water vapour.
6.3	80.5	110	765	34—39.6°	0.12—0.14
4.8	80.5	103	768	32—36	0.10—0.13
4.9	80.5	100	768	32—36	0.10—0.13
7.45	82.4	143	775	36—42	0.07—0.12

In the experiments described in the foregoing pages, the drying of the gas mixtures used was not carried to an extreme degree. It has been shown by Baker (J., 1902, 81, 7, 400) that considerably more thorough drying is necessary to prevent the combination of hydrogen and oxygen than that of carbon monoxide and oxygen. It seemed desirable, therefore, to find whether the catalysing influence of hydrogen on the combination of carbon monoxide and oxygen would be affected by a more thorough drying of the gas mixture. Experiments were accordingly carried out in the same way as those already described, but with considerably more intense and prolonged drying of the apparatus, as rapid filling as possible, and more protracted exposure of the gases to phosphoric oxide. The results are in Table V.

TABLE V.

	Volume of gas, c.c.	% Volume of hydrogen.	Time of drying.	Result of first sparking.	Sparking on addition of undried air.
1.	4.5	0.043	12 weeks	No ignition	Ignition
2.	4.2	0.040	19 „	No ignition	Ignition
3.	4.2	0.042	20 „	No ignition	Ignition

Since in all cases the admission of a small bubble of undried air to these mixtures made them ignitable by the spark, it appears from these experiments that the catalytic action of hydrogen is conditioned by the presence of a minimal quantity of water vapour.

*Variation of Electrodes.*—With a view to find whether a change in the material of the electrodes would reveal anything of interest, eudiometers were made with electrodes of copper, nickel, silver, and gold. After the usual experimental procedure, it was found in all cases that the results were the same as those obtained by the use of the eudiometers with platinum electrodes. In these experiments, the difficulty of sealing metals directly into glass was overcome by the use of seals of "red platinum" (copper deposited electrolytically on a nickel alloy).

*General Observations on the Results.*—It is, of course, to be understood that the significance of the numerical results recorded in this paper may be considerably restricted by the particular conditions of the experiments. Slight variation in procedure and especially in the conditions of spark ignition may be suspected to have far-reaching effects. Experiments now in progress have shown that the effective proportion of the catalyst gases varies considerably with the length of the spark gap and the character of the discharge. But, working within the conditions described, precautions have been taken to interchange the eudiometers used respectively for the hydrogen and the water vapour additions, and to change the material of the electrodes.

### *Summary.*

A comparison has been made of the relative influence of hydrogen and water vapour on the ignitability of a mixture of carbon monoxide and oxygen by the spark discharge. To the purified gases, mixed in combining proportions and contained in two eudiometers, hydrogen and water vapour were added in equivalent proportion, and after time had been allowed for admixture a spark was passed simultaneously in series through each mixture.

It appeared in the first instance, when the drying of the carbon monoxide-oxygen mixture had not been greatly prolonged, that hydrogen was more effective than water vapour in conferring ignitability. Through a range of concentrations varying from approximately 0.03 to 0.06%, hydrogen was effective, whilst water vapour was not. An estimation of the minimum quantities necessary gave 0.03% for hydrogen and 0.12% for water vapour. These figures are not to be taken as absolute values, for they are affected by the particular conditions of the experiments.

In later experiments with more intensive drying of the com-

bustible mixture, it was found that the activity of the hydrogen was altogether inhibited. In other words, the superior catalytic effectiveness of hydrogen just described was in its turn conditioned by the presence of a minimal quantity of water vapour. It may equally well be said, alternatively, that in the presence of hydrogen a minimal quantity of water sufficed to confer ignitability.

These results are in harmony with our earlier observations and with those of other workers.

[Received, November 27th, 1929.]

## XXVI.—*The Effect of Hydrogen-ion Concentration on the Electrode Potential of Iron.*

By A. L. MCAULAY and GEOFFREY L. WHITE.

CORROSION of iron in practical cases is almost entirely due to the electrolytic effect of currents flowing between points on its surface which are in different electrical conditions. A trace of moisture on the surface is sufficient to permit corrosion to take place in this manner. The existence of such differences in electrode potential is known to be caused to a great extent by differences in exposure to oxygen of adjoining regions in the corroding iron. It is also known that the electrode potential of iron varies greatly with other external conditions, and it is important to know what effect the variation of some of these conditions will produce. The two most powerful factors in determining the behaviour of a corroding iron surface are (i) exposure to oxygen, and (ii) the hydrogen-ion concentration of the electrolyte causing corrosion.

It was thought that an investigation of the electrical behaviour of iron surfaces under varying conditions of  $p_H$  would give information of fundamental importance, provided that the initial difficulties in the realisation of a standard reproducible state could be overcome. It was further hoped that, with rigorously simplified conditions, results of theoretical interest might be obtained which would throw light on the general mechanism of the production of electrode potentials.

A previous investigation (McAulay and Bastow, J., 1929, 85) led to the recognition of a standard condition in neutral solutions, and gave the results of varying the degree of exposure to oxygen of a surface brought to this standard state. The present paper is mainly concerned with an investigation of the effect of varying hydrogen-ion concentration on electrode potential in an air-free solution. The results differed according to the anion present, but

were completely reproducible with the two anions (chloride and phosphate) investigated. Further experiments were carried out in solutions in a normal state of aeration; here no attempt was made to obtain accurate quantitative reproducibility, but certain large-scale effects are described which were qualitatively reproducible. In particular, conditions were observed where, with an extremely small change in  $p_{\text{H}}$ , a very great change in electrode potential was brought about.

#### EXPERIMENTAL.

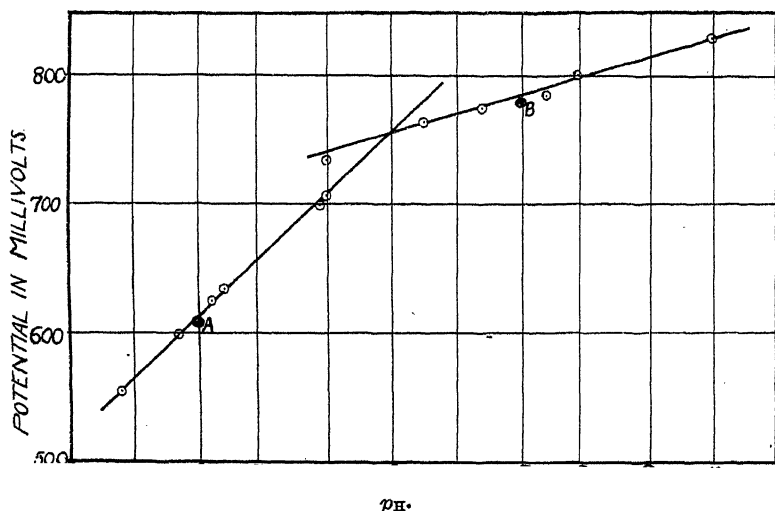
The apparatus and experimental technique for obtaining an iron electrode in an air-free solution and for measuring its potential were the same as in the previous paper (*loc. cit.*). *M/5*-Solutions of potassium chloride and potassium phosphate were used, and the  $p_{\text{H}}$  was lowered by adding to each its appropriate acid, or raised by adding sodium hydroxide. The  $p_{\text{H}}$  naturally altered when the unbuffered solutions in the neighbourhood of neutrality were boiled; and it also changed, when on the acid side, owing to dissolution of oxide from the electrode. The solution was tapped and the  $p_{\text{H}}$  measured when equilibrium had been reached and the electrode was at a steady potential. The  $p_{\text{H}}$  measurements were made by the use of appropriate indicators standardised by solutions of the B.D.H. Universal Buffer, which were in their turn standardised with a hydrogen electrode, as it was found that they changed considerably with time. Some difficulty was experienced in obtaining steady conditions when the electrolyte was alkaline, probably owing to a decreasing tendency for destruction of the oxide film formed on the electrode before immersion. Up to a  $p_{\text{H}}$  of about 10, this difficulty could be overcome by the passage of a quantity of electricity of the order of 100 millicoulombs to the electrode as cathode. The electrode would in these conditions polarise to a high negative potential (of the order of 1.0 volt on the saturated calomel scale) and, when this polarisation had disappeared, would be found to be in a steady reproducible condition. The inconsistency between this effect of current and that found in the case of neutral solutions described in the earlier paper is a real one, and it is intended to make this and certain other peculiarities the subject of further investigation.

At higher alkalinity than  $p_{\text{H}}$  10, it was not possible to bring iron to an electrically reproducible state. The electrode then showed all the features associated with the presence of a film of oxide, gradually drifting to an indeterminate potential of the order of  $-0.4$  on the standard calomel scale.

## Results.

(a) *In air-free solutions.* Fig. 1 shows the relation between  $p_H$  and equilibrium electrode potential of pure iron\* against the saturated calomel electrode. Fig. 1(a) represents points given by potassium chloride and Fig. 1(b) those given by potassium phosphate. The solution was  $M/5$  in anion concentration, with the exception of the most acid point on the chloride curve and of the two check points A and B in Fig. 1(a).

FIG. 1 (a).



Equilibrium potentials (saturated calomel scale) in  $N/5\text{-KCl}$  (point A, electrolyte =  $N/100\text{-Cl'}$ ; point B, electrolyte =  $4.2N\text{-Cl'}$ .)

These final equilibrium potentials required very different times for their establishment. The rise in the extreme alkaline region was very slow indeed, and the slightest trace of oxygen would prevent an equilibrium potential being reached, presumably owing to the formation of an oxide film which caused the potential to drift to a more positive value than the equilibrium potential. Difficulties of a different sort were encountered in the acid region, where the potential tended to become unsteady at a higher value than the equilibrium potential. In the neutral region with chloride solutions, difficulty was experienced in maintaining the  $p_H$  constant and in measuring its true value in the cell. Occasionally, in

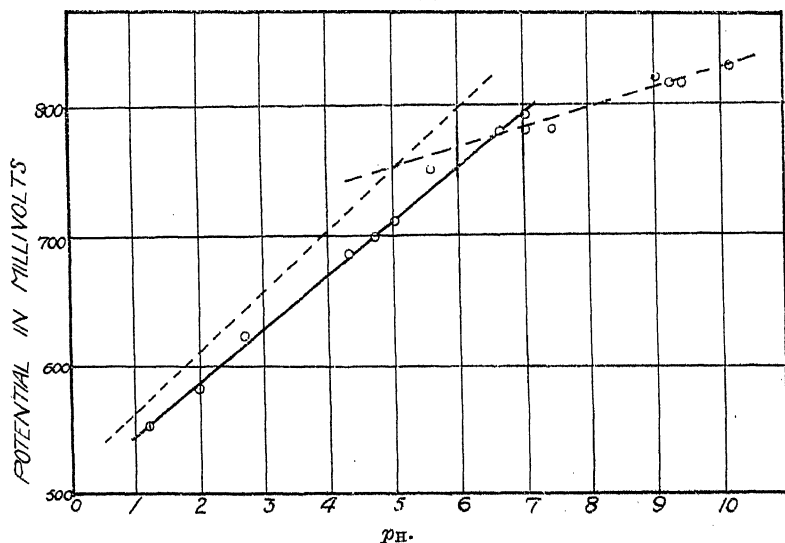
\* The iron electrodes were supplied by Hilger and the following analysis given: Sn, 0.02; Pb, 0.001; As, 0.005; P, 0.010; Mn, 0.031; Mo, 0.05; Cu, 0.04; Ni, 0.007; Cr, 0.016%; Si and Sb, traces; Al, Mg, Ca, Ti, V, none; Co is not mentioned.



making check experiments, an indicator was introduced into the cell.

It will be seen that in each case the relation between  $p_H$  and equilibrium electrode potential is expressed fairly exactly by a pair of straight lines, the one of less slope in the alkaline region being the same for both anions, but that in the acid part being specific for each anion. A tentative explanation is attempted later.

FIG. 1 (b).



Equilibrium potentials (saturated calomel scale) in  $M/5$ -phosphate solutions.  
[The broken lines are reproduced from Fig. 1 (a).]

In order to test whether the concentration of the anion had any effect on the potential at a given  $p_H$ , experiments were made with concentrations of  $N/100$ - and of  $4.2N$ -potassium chloride [points A and B, respectively, Fig. 1(a)]. In both cases the equilibrium values are seen to be practically on the curve, although peculiarities were noticeable in their establishment.

(b) *In solutions not rendered air-free.* The behaviour of electrodes in such solutions was so complicated that no standard quantitative work was attempted. Certain large-scale effects were observed, however, which seem to be of importance. In phosphate solutions, a definite critical  $p_H$  exists (between 7.5 and 8.5) on the alkaline side of which the equilibrium potential of a freshly-ground electrode starts at about  $-0.31$  (saturated calomel scale) but falls in about 10 mins. to about  $-0.3$ , at which it remains constant; on the acid

side, however, the potential rises rapidly to the neighbourhood of  $-0.8$  and then remains constant. In chloride solutions no such critical  $p_H$  for equilibrium potentials exists: for solutions as alkaline as  $p_H 9$  the potential very slowly drifts to a value near  $-0.7$ .

### *Discussion of Results.*

(a) *Air-free Experiments.*—The following tentative theory is advanced to explain the results shown in Fig. 1. The steeper straight line on the acid side of the curve represents the deposition of hydrogen by direct replacement of iron, the electrode in this region behaving directly as a hydrogen electrode with high negative potential due to overvoltage. This theory views the deposition of hydrogen as similar to its electrolytic deposition. The stream of ferrous ions leaving the metal and balancing the positive current caused by the hydrogen is thought to have no effect on the overpotential. Experiments on the simultaneous deposition of metal and hydrogen ions suggest that this should be the case (McAulay and Bowden, *Phil. Mag.*, 1926, **1**, 1282).

This theory immediately accounts for the fact that the slope of the line is less than  $0.057$  volt per  $p_H$  unit, for hydrogen evolution is more rapid the higher the concentration of the acid. It also accounts for the different lines obtained with chloride and phosphate. In the first case, deposition takes place at a clean iron surface, and in the second, at a surface of insoluble ferrous phosphate, and the overvoltage would be expected to have a different value.

There seems considerable difficulty in explaining the less steep straight line representing the more alkaline part of the curve, where evolution of bubbles does not take place. It is thought that it is determined by hydrogen overpotential and that the iron is effectively a hydrogen electrode. If the potential were determined by ferrous ions depositing on a clean iron surface, it would be at least  $0.2$  volt more negative than that observed; while ferric ions would be deposited till a concentration of less than  $10^{-15}N$  was left in solution before they could be in equilibrium with an iron surface at this potential. The electrode cannot be acting as an oxidation-reduction electrode for ferrous and ferric ions, for the concentration of ferric ions at such a potential would have to be of the order  $10^{-20}$  of that of the ferrous ions. It is impossible to conceive of such minute traces of an ion in the electrolyte determining the potential of the electrode when there is nothing to prevent the solution of ferrous ions from the iron. It appears probable, therefore, that hydrogen determines the electrode potential.

Another possibility is that the electrode surface throughout this part of the curve is in a different condition from that in which

there is direct replacement of iron by hydrogen, and that it has not the character of a clean iron surface. Possibly, the observed potential is characteristic of the equilibrium between ferrous ions in the solution and ferrous ions in some oxide lattice on the electrode surface. It is hoped that experiments with other metals will afford information as to the reason for this different slope.

(b) *Experiments in Solutions not rendered Air-free.*—The explanation of the qualitative results observed with these solutions is believed to be as follows. In the case of the phosphate, the definite positive potential obtained at  $p_H$  values greater than 8.5 is due to the formation of an oxide skin which the feeble disintegrating powers of the phosphate ion are unable to destroy. The negative potential obtained at smaller  $p_H$  values is believed to be due to the formation of a film of insoluble ferrous phosphate. The chloride ions, on the other hand, have a powerful disintegrating effect on the oxide film, and the final potential observed in aerated solutions is the result of the opposing effects of destruction of the film by chloride ions and its repair by dissolved air. Experiments with potassium sulphate indicated a much less energetic disintegration of the film by sulphate ions than by chloride ions.

#### *Summary.*

Examination of the electrode potentials of pure iron in air-free solutions of various  $p_H$  containing potassium chloride or phosphate has led to results of a standard and reproducible nature, which should provide a foundation for work of a more directly practical nature where conditions are necessarily more complicated. The curves showing the relation between  $p_H$  and equilibrium potential split up into two straight lines of different slope, and a discussion of these is attempted.

Experiments have also been made with solutions not rendered air-free, and a very marked discontinuity of the curves has been observed in the case of the phosphate solutions.

In conclusion, our best thanks are due to the Commonwealth Council for Scientific and Industrial Research for the generous grant that we have received from them which has made it possible to carry out the work described in this paper. In addition, attention is drawn to an oversight in a previous paper on this subject (J., 1929, 85), where it was intended to make a similar acknowledgment of an earlier grant made for the same purpose by the C.S.I.R.

## XXVII.—*The Pyrophosphate Method for the Determination of Magnesium.*

By STANKO STANKOV MIHOLIĆ.

It is known that in the determination of magnesium as pyrophosphate great care is necessary to obtain a precipitate of the composition  $\text{MgNH}_4\text{PO}_4$  (Epperson, *J. Amer. Chem. Soc.*, 1928, **50**, 321) and that it is necessary to ensure that ignition yields pure magnesium pyrophosphate free from organic matter. Various devices for obtaining the product white have been suggested (McNabb, *ibid.*, p. 301; Hillebrand, *Bull. Geol. Survey, U.S.A.*, 1919, **700**, 151), but Epperson has shown that these expedients are of little value. Since platinum crucibles are expensive and may be damaged, it is desirable to utilise porcelain or sintered-glass crucibles. In this case, however, lower temperatures of ignition must be used. Theoretical considerations lead to the conclusion that the temperature necessary for a complete dissociation of  $\text{MgNH}_4\text{PO}_4$  cannot be so high as hitherto used, viz., 900—1200°. Most ammonium salts dissociate below 500°, and ortho- is transformed into pyro-phosphoric acid at or below 250°. Moreover, it is a common experience that the charring of organic material is the more complete, and the ash the whiter, the lower the temperature used. Further, McNabb (*J. Amer. Chem. Soc.*, 1927, **49**, 1451) has shown that the analogous dissociation of magnesium ammonium arsenate is complete at 500—600°. An attempt was therefore made to ignite magnesium ammonium phosphate at as low a temperature as possible, and 480° was chosen as being probably the most suitable.

### EXPERIMENTAL.

For filtration, the sintered Jena-glass crucibles used (No. 3, with an average pore diameter of 20—30  $\mu$ ) were very satisfactory: one of them was used 50 times, and is still in use, showing only a slight corrosion and having lost only 0.021 g. owing to repeated cleaning with concentrated hydrochloric acid.

The tests were made with *N*/20-solutions of magnesium chloride or sulphate as standard. The magnesium content of the former was checked by evaporation with yellow mercuric oxide, ignition, and weighing as magnesium oxide, or by evaporation with sulphuric acid and weighing as magnesium sulphate; for the latter standard, only the second method was used, the other method being impracticable. As the magnesium sulphate solution was slightly too concentrated, corrected values for the calculated amount of pyrophosphate were substituted in Tables II and III.

The details of the estimation were as follows. To a measured amount of the solution, diluted with 200 c.c. of water, were added 3 drops of concentrated hydrochloric acid and then a filtered solution of 0.5 g. of ammonium chloride and 1 g. of ammonium phosphate in 20 c.c. of water containing 2 or 3 drops of a 1% alcoholic solution of phenolphthalein. The mixture was heated to boiling, and aqueous ammonia was added slowly drop by drop until the colour remained pink after prolonged stirring, followed by 50 c.c. of ammonia solution ( $d$  0.96) while the mixture was still hot. After standing over-night, the liquid was filtered through a sintered-glass crucible, the precipitate washed with about 50 c.c. of 2½% ammonium hydroxide solution, heated in an electric oven at 480° for 2 hours, and weighed. Subsequent heatings at the same temperature and weighings showed that the precipitate had attained constant weight in the first heating: it was a light snow-white powder. The results are in Tables I, II, and III.

TABLE I.

N/20-Solution of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  used. Single precipitation.

10 c.c.		20 c.c.		50 c.c.	
$\text{Mg}_2\text{P}_2\text{O}_7$ calc., 0.0557 g.		$\text{Mg}_2\text{P}_2\text{O}_7$ calc., 0.1114 g.		$\text{Mg}_2\text{P}_2\text{O}_7$ calc., 0.2785 g.	
$\text{Mg}_2\text{P}_2\text{O}_7$ found, g.	Diff., g.	$\text{Mg}_2\text{P}_2\text{O}_7$ found, g.	Diff., g.	$\text{Mg}_2\text{P}_2\text{O}_7$ found, g.	Diff., g.
0.0545	-0.0012	0.1100	-0.0014	0.2770	-0.0015
0.0541	-0.0016	0.1098	-0.0016	0.2770	-0.0015
0.0551	-0.0006	0.1117	+0.0003	0.2775	-0.0010
0.0556	-0.0001	0.1107	-0.0007	0.2770	-0.0015
0.0556	-0.0001	0.1102	-0.0012	0.2778	-0.0007
0.0551	-0.0006	0.1105	-0.0009	0.2783	-0.0002
0.0550*	-0.0007*	0.1105*	-0.0009*	0.2774*	-0.0011*
Average error, -1.26%.		Average error, -0.81%.		Average error, -0.39%.	

\* Mean.

TABLE II.

N/20-Solution of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  used. Single precipitation.

5 c.c.		25 c.c.		50 c.c.	
$\text{Mg}_2\text{P}_2\text{O}_7$ calc., 0.0284 g.		$\text{Mg}_2\text{P}_2\text{O}_7$ calc., 0.1420 g.		$\text{Mg}_2\text{P}_2\text{O}_7$ calc., 0.2839 g.	
$\text{Mg}_2\text{P}_2\text{O}_7$ found, g.	Diff., g.	$\text{Mg}_2\text{P}_2\text{O}_7$ found, g.	Diff., g.	$\text{Mg}_2\text{P}_2\text{O}_7$ found, g.	Diff., g.
0.0293	+0.0009	0.1415	-0.0005	0.2845	+0.0006
0.0297	+0.0013	0.1404	-0.0016	0.2852	+0.0013
0.0286	+0.0002	0.1408	-0.0012	0.2838	-0.0001
0.0284	±0.0000	0.1409	-0.0011	0.2848	+0.0009
0.0283	-0.0001	0.1404	-0.0016	0.2850	+0.0011
0.0281	-0.0003	0.1406	-0.0014	0.2848	+0.0009
0.0287*	+0.0003*	0.1408*	-0.0012*	0.2850*	+0.0011*
Average error, +1.06%.		Average error, -0.85%.		Average error, +0.39%.	

\* Mean.

TABLE III.

*N*/20-Solution of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  used. Double precipitation.

Amount of solution taken, 50 c.c. $\text{Mg}_2\text{P}_2\text{O}_7$ , calc., 0.2839 g.			
$\text{Mg}_2\text{P}_2\text{O}_7$ , found, g.	Diff., g.	$\text{Mg}_2\text{P}_2\text{O}_7$ , found, g.	Diff., g.
0.2841	+0.0002	0.2848	+0.0009
0.2843	+0.0004	0.2848	+0.0009
0.2843	+0.0004	0.2847	+0.0008
		Mean 0.2845	+0.0006

Average error, +0.21%.

Tables II and III show that scarcely any alteration is effected by reprecipitation of the double phosphate.

In order to ascertain whether the conversion into pyrophosphate was complete at  $480^\circ$ , 0.2 g. samples of the pyrophosphate obtained were heated for  $\frac{1}{2}$  hour in a platinum crucible by a blast burner; the powder sintered to a hard crumbly mass, but the losses in four cases were 1.7, 1.7, 1.3 and 1.4 mg., giving an average of 1.5 mg. or 0.75%.

The method described above proved satisfactory in a long series of determinations of magnesium in mineral waters.

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## XXVIII.—*The Absorption Spectra of Diphenyl and Some Derivatives.*

By THOMAS C. C. ADAM and ALFRED RUSSELL.

IN connexion with the relations between the constitution of organic compounds and their absorption spectra, it was shown (Baly, Edwards, and Stewart, J., 1908, **93**, 1902) that the seven-banded absorption spectrum of benzene can be explained by Collie's oscillation theory (J., 1897, **71**, 1013) for the structure of the benzene molecule on the assumption that each band corresponds to a make-and-break of valency. The spectrum of naphthalene was discussed in a similar manner (Baly and Tuck, J., 1906, **89**, 514) and found to be in agreement.

In the course of the following work, the resemblance manifest between the spectra of diphenyl and of its derivatives has led to a corresponding theory for this hydrocarbon. Since one carbon atom of each nucleus is bound, no valency oscillation involving only two carbon atoms can take place, nor is an oscillation

involving all six carbon atoms possible. Three types of pulsation remain :

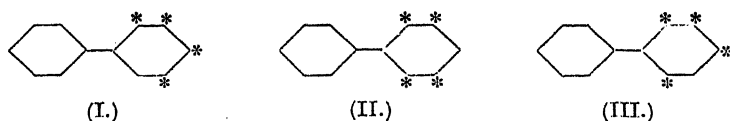
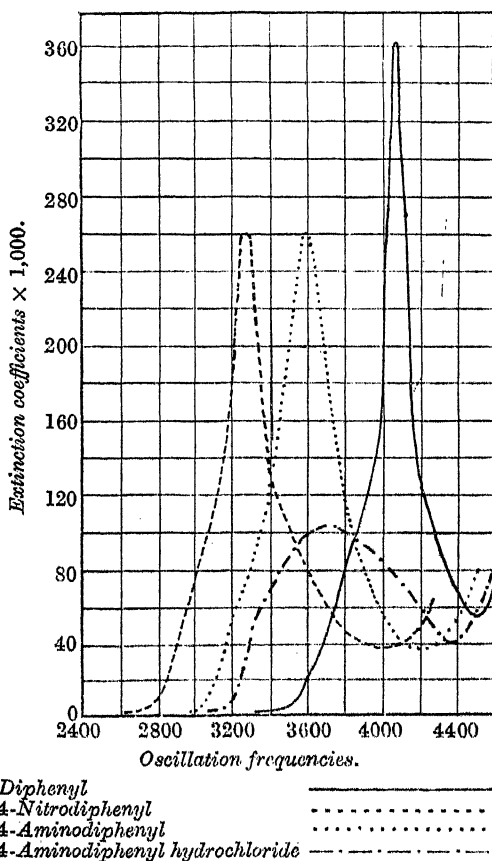


FIG. 1.



If the appearance of a band in the spectrum is to indicate a make-and-break of valency, then only one of these is possible. The same band is shown by the 4-derivatives as by diphenyl itself, an indication that the pulsation of the molecule does not include the carbon atom in the 4-position; that is, the oscillation of valency is taking place as in (II). The spectroscopic evidence thus points to the existence of a virtual para bond in the diphenyl molecule making the

4-carbon atom the stable member of the ring. The spectra obtained for the 2-derivatives bear out the theory in the following respects:

(1) The 4-carbon atom being partially bound by a virtual bond, any electronic disturbance which includes this atom will be small compared with the typical disturbance, and the resulting band will

be absorbed in the typical band.

(2) If the main pulsation is suppressed by a 2-substituent, then selective absorption will be eliminated, except in so far as the 4-carbon atom is free to oscillate. In practice, 2-nitrodiphenyl shows one shallow band, and the heavily substituted 2-2''-diphenyldiphenyl shows a band still shallower.

#### EXPERIMENTAL.

The solvent employed was, in most cases, spectroscopically pure ethyl alcohol. For 4-diphenyldiphenyl and 4'-nitro-4-diphenyldiphenyl, it was necessary to employ redistilled A. R. chloroform owing to the low solubility in alcohol.

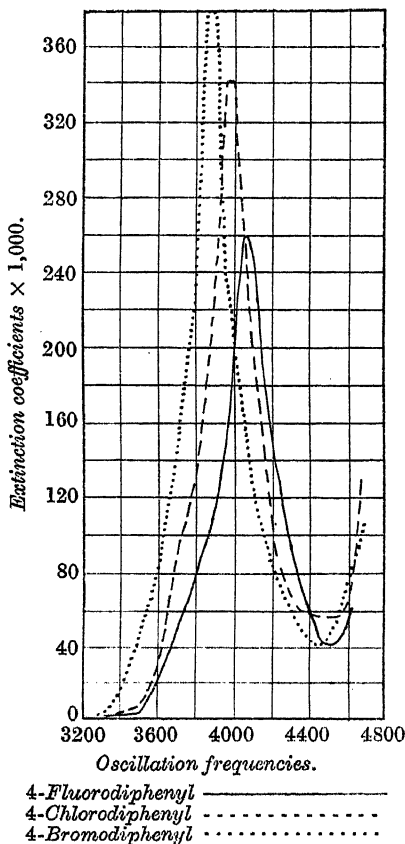
The spectra were photographed with a Hilger Model 3 all-quartz ultra-violet spectrograph with rotating sector attachment. The persistence of the band is taken as being the difference between the extinction coefficients of the head of

the band and of that frequency, towards the violet end, where complete transmission is obtained.

*Diphenyl*, m. p. 70.5°. The spectrum shows a deep well-defined band with its head at  $\nu$  4063 (see Fig. 1), in good agreement with the measurement of Baly and Tryhorn (J., 1915, 107, 1058), who examined the spectrum of a thin film of diphenyl.

*4-Nitrodiphenyl*, m. p. 113°. Substitution of a nitro-group for hydrogen has moved the head of the band towards the red to  $\nu$  3259.

FIG. 2.





*4-Aminodiphenyl*, m. p. 53°. The amino-substituent has the effect of broadening the band. The size and mass of the group being less than in the previous instance, the band head has not been shifted to the same extent, maximum absorption occurring at  $\nu$  3590.

*4-Aminodiphenyl hydrochloride*. The reduction of reactivity consequent on the formation of the hydrochloride brings about a considerable decrease in the persistence of the absorption, in this case from 224 to 64 units. The head of the band has also moved back towards the ultra-violet to  $\nu$  3720.

*4-Fluorodiphenyl*, m. p. 74.5°. As might be expected, the entry into the diphenyl molecule of a small light atom such as fluorine has no appreciable effect on the absorption (see Fig. 2).

*4-Chlorodiphenyl*, m. p. 75.5°. In this case, the greater size and mass of the chlorine atom has shifted the position of maximum absorption to  $\nu$  3979. The band is also more persistent, although the configuration of the curve is unaltered.

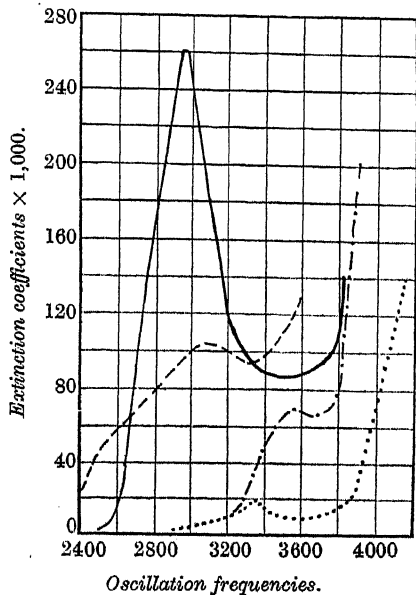
*4-Bromodiphenyl*, m. p. 89°. Replacement of chlorine by bromine has the effect of moving the head of the band to  $\nu$  3892.

*4-Diphenyllyldiphenyl*, m. p. 260°. Spectroscopically, at least, this compound acts as a heavily substituted diphenyl. The band, while retaining the characteristics of the diphenyl band, is shallower with a persistence of 172. The head has moved well up towards the red, occurring at  $\nu$  2965.

*4'-Nitro-4-diphenyllyldiphenyl*, m. p. 274°. Although no definite band is shown, there is evidence of a very shallow band about  $\nu$  3050.

*2-Nitrodiphenyl*, m. p. 36°. The feeble valency oscillation per-

FIG. 3.



*4-Diphenyllyldiphenyl*

*4'-Nitro-4-diphenyllyldiphenyl*

*2-Nitrodiphenyl*

*2-2''-Diphenyllyldiphenyl*

missible in a 2-substituted diphenyl is demonstrated in this case by the appearance of a very shallow band at  $\nu$  3350.

2-2''-Diphenylaldiphenyl, m. p.  $185^\circ$ . In conformity with the theory, the selective absorption shown by this compound is small, a very shallow band with its head at  $\nu$  3550 being obtained.

We are grateful to Messrs. Imperial Chemical Industries for a grant defraying the cost of the work.

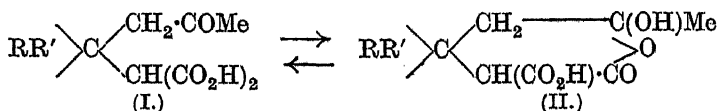
THE SIR DONALD CURRIE LABORATORIES,  
THE QUEEN'S UNIVERSITY,  
BELFAST.

[Received, November 18th, 1929.]

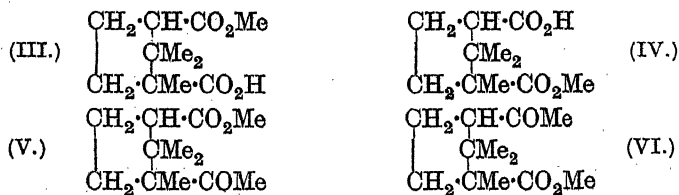
XXIX.—*Studies in Keto-lactol Tautomerism. Part IV. Chemistry of 5-Acetyl-1:1:2-trimethylcyclopentane-2-carboxylic Acid. Observations on the Constitutions of the Acid Esters of Camphoric Acid, and a Synthesis of Homoepicamphor.*

By MUHAMMAD QUDRAT-I-KHUDA.

IN extending the study of ring-chain tautomerism of the keto-lactol type (I and II) to keto-monocarboxylic acids, it was suggested (J., 1929, 205) that the evidence of the existence of the hydroxy-phase of such acids would be obtained more readily by an investigation of  $\delta$ -keto-monocarboxylic acids having substituents at the  $\beta$ - and the  $\gamma$ -carbon atom. The  $\delta$ -keto-acids derived from the acid esters of camphoric acid fulfil this condition and their behaviour has been examined.



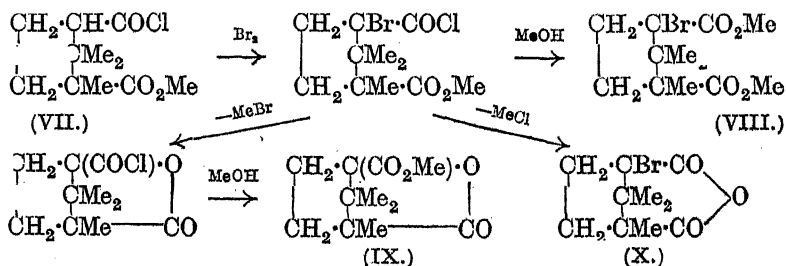
*ortho*-Methyl hydrogen camphorate (III) and *allo*-methyl hydrogen camphorate (IV), m. p.  $77^\circ$  and  $86^\circ$  respectively, when converted



into their acid chlorides and acted on by zinc methyl iodide under parallel conditions, gave, not methyl 2-acetyl-1:1:2-trimethyl-

cyclopentane-5-carboxylate (V, from III) and methyl 5-acetyl-1:1:2-trimethylcyclopentane-2-carboxylate (VI, from IV), but only one keto-ester; the semicarbazones obtained from specimens prepared from both sources melted, separately or mixed, at the same temperature.

The fact that only one keto-ester was obtained from the isomeric acid esters suggested that these were structurally identical and differed only in the spatial arrangement of the groups: this view was supported by the results obtained on brominating the acid chlorides produced from the two acid esters. Both chlorides absorbed bromine with almost equal ease and the products isolated after the reaction mixture had been poured into methyl alcohol were methyl camphanate (IX),  $\omega$ -bromocamphoric anhydride (X), and small quantities of the bromo-ester (VIII) and camphanic acid. These facts, particularly the production of the bromo-ester (VIII), suggest that the *allo*- and the *ortho*-acid ester both have the carboxyl group attached to a tertiary carbon atom and that the bromination proceeds in the normal way; the intermediate product ultimately loses methyl bromide and methyl chloride, giving the ester of camphanic acid and bromo-camphoric anhydride:

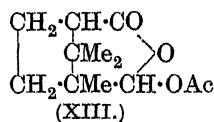
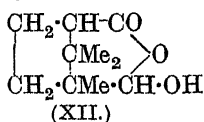
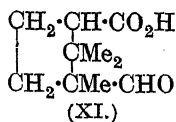


The structural identity of the two acid esters is rendered very probable by the fact that, when the *ortho*-acid ester (m. p. 77°) is converted into the acid chloride by heating with thionyl chloride and then treated with water, the product obtained melts at the same temperature as *allo*-methyl hydrogen camphorate; its crystalline structure is identical with that of the latter and there is no depression of the melting point of a mixture of the two compounds.

In view of these facts the work of Walker and his collaborators (Walker, J., 1893, **63**, 495; Walker and Henderson, J., 1895, **67**, 337; Walker and Cormack, J., 1900, **77**, 374), Noyes and Blanchard (*Amer. Chem. J.*, 1901, **26**, 285), and Haller and Blanc (*Compt. rend.*, 1905, **141**, 697) requires revision, which is being undertaken.

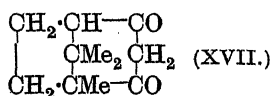
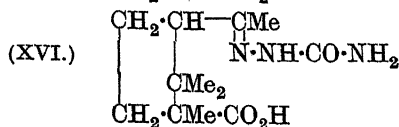
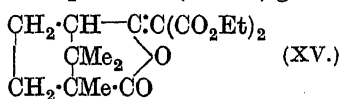
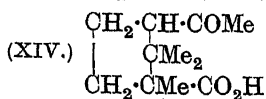
Camphoraldehydic acid (XI) (Bredt, *J. pr. Chem.*, 1917, **95**, 63), when heated with acetic anhydride, gives an acetoxo-derivative

(XIII), the reaction taking place with the isomeric hydroxy-lactonic form (XII) of the aldehydic acid.

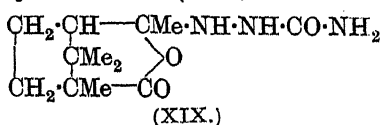
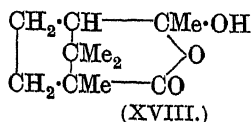


The keto-acid (XIV) shows similar properties.

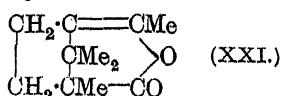
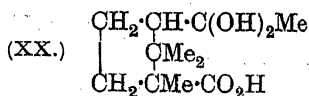
The ester (VI) on treatment with alcoholic potassium hydroxide gave a mixture of two solids, *viz.*, the *keto-acid* (XIV) and a *diketo*-compound (XVII), and a liquid substance, which was apparently the hydroxy-lactonic form (XVIII) of the keto-acid (XIV). The same keto-acid appears to have been obtained by Winzer (*Annalen*, 1890, 257, 298) from the product of hydrolysis of camphorylmalonic ester (XV). On treatment with semicarbazide acetate, the acid (XIV) gave a crystalline *semicarbazone* having the properties of the normal compound (XVI), whereas the liquid acid (XVIII) gave an



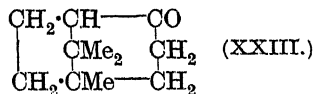
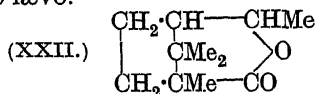
isomeric *substance*, of indefinite crystalline structure and very soluble in alcohol (compare the addition compound of Balbiano's acid and phenylhydrazine; Mahla and Tiemann, *Ber.*, 1895, 28, 2151), probably to be represented by the formula (XIX) :



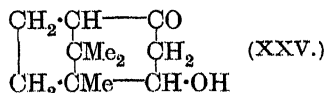
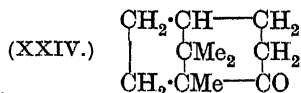
When the keto-acid (XIV) or the hydroxy-lactone (XVIII) was treated with acetyl chloride, very little neutral product was obtained; the material was recovered in a *hydrated* form (XX), which was converted into the keto-acid (XIV) on drying. Both the keto-acid and the hydroxy-lactone, however, when treated with acetic anhydride, were converted into the same unsaturated *lactone* (XXI), which still exhibited optical activity although one of the two asymmetric carbon atoms had lost its asymmetry.



The keto-acid (XIX), on reduction with sodium and alcohol, gave *methylcampholide* (XXII): the introduction of the third asymmetric carbon atom changed the direction of rotation from dextro to lævo.



The keto-ester (VI), when heated with alcoholic sodium ethoxide, was converted into the diketo-compound (XVII), which, as already mentioned, was also obtained in small quantity by hydrolysis of the ester. The reduction of the diketo-compound by Clemmensen's method gave a waxy mass, with a strong camphoraceous odour, consisting of a ketone and a second substance. The ketone, produced in very small quantity, forms a *semicarbazone*, m. p. 220°, isomeric with the semicarbazone of homocamphor (XXIV), m. p. 250° (Lapworth and Royle, J., 1920, 117, 743), and is provisionally regarded as homocopicamphor (XXIII). The second substance is probably the keto-alcohol (XXV); it could not be obtained sufficiently pure for analysis.



Experiments are now in progress on the action of potassium cyanide on the lactone (XXII); it is also hoped to prepare the ketone (XXIII) and the keto-alcohol (XXV) in quantity in order to settle their constitutions.

#### EXPERIMENTAL.

*ortho*-Methyl hydrogen camphorate was prepared by Walker's method (*loc. cit.*). After crystallising twice from light petroleum (b. p. 40—60°), it melted at 77° and had  $[\alpha]_D^{25} + 53.94^\circ$  in 2.95% alcoholic solution.

*allo*-Methyl hydrogen camphorate was obtained by Walker's method (*loc. cit.*) by the partial hydrolysis of methyl camphorate, prepared by a method based on the one used by Frankland and Aston (J., 1901, 79, 517) for the esterification of tartaric acid and also by the method recommended by Haller and Blanc (*loc. cit.*). After crystallising twice from petroleum (b. p. 60—80°), the *allo*-ester melted at 86° and had  $[\alpha]_D^{25} + 45.1^\circ$  in 4.3% alcoholic solution.

*Bromination of the Chloride of the allo-Ester.*—The acid ester (42 g.) was mixed with phosphorus pentachloride (41 g.). When the vigour of the reaction had abated, the mixture was heated at 75—80° for an hour, 12 c.c. of dry bromine were gradually added, and

the heating was continued for 4—5 hours. The excess of bromine was then evaporated and the reaction mixture was poured into methyl alcohol (150 c.c.) and heated on the steam-bath for some time. After most of the alcohol had evaporated, the residue was poured into water and shaken with ether. The extract was washed with sodium carbonate solution and dried, and the solvent removed. The residue, consisting of crystalline material mixed with a little oil (A), was triturated with petroleum. The solid then remaining was partly soluble in hot petroleum (b. p. 60—80°); on cooling, the solution deposited methyl camphanate, m. p. 110° after recrystallisation (Found: C, 62.1; H, 7.5. Calc. for  $C_{11}H_{16}O_4$ : C, 62.3; H, 7.5%), hydrolysis of which gave camphanic acid, m. p. 201° (compare Bredt, *Annalen*, 1913, 395, 39). The portion of the solid insoluble in hot petroleum crystallised well from chloroform, melted at 215° (Found: Br, 30.8. Calc. for  $C_{10}H_{13}O_3Br$ : Br, 30.7%), and had all the properties of Wreden's bromocamphoric anhydride (*Annalen*, 1872, 163, 332).

The oil (A) was recovered from the petroleum solution and distilled in a vacuum: a little methyl camphorate came over and then methyl bromocamphorate distilled at 162—164°/12 mm. with slight decomposition. The yield was very small and the bromo-ester was not pure (Found: Br, 25.0.  $C_{12}H_{19}O_4Br$  requires Br, 26.0%).

The above sodium carbonate extract on acidification gave an oil which, when hydrolysed with caustic soda, yielded camphoric acid and a small quantity of camphanic acid.

The products obtained in a similar way from *ortho*-methyl hydrogen camphorate were essentially of the same nature as the above.

*Conversion of ortho- into allo-Methyl Hydrogen Camphorate.*—The *ortho*-ester (7 g.) was treated with thionyl chloride (4 c.c.) at 70—75° for an hour, the excess of thionyl chloride then removed under reduced pressure, and the residue diluted with dry benzene (50 c.c.) and decomposed with water. The acid was extracted with dilute sodium carbonate solution, precipitated by acidification with hydrochloric acid, and extracted with ether. After drying and removal of the ether, the oily residue obtained partly solidified on cooling. The solid was separated from the oily impurities by trituration with petroleum and crystallised from the same solvent; it then melted at 86° (Found: C, 61.5; H, 8.6. Calc. for  $C_{11}H_{18}O_4$ : C, 61.7; H, 8.4%).

The *allo*-ester, when similarly treated, was recovered unchanged.

*Methyl 5-Acetyl-1 : 1 : 2-trimethylcyclopentane-2-carboxylate* (VI).—*ortho*-Methyl hydrogen camphorate was mixed with thionyl chloride (15 c.c.) and the acid chloride obtained after the removal of the

excess of thionyl chloride as stated above was cooled, diluted with an equal volume of dry benzene, and added to a cold solution of zinc methyl iodide prepared from methyl iodide (35 c.c.), ethyl acetate (18 c.c.), and zinc-copper couple (35 g.) in benzene solution in the usual way. The *keto-ester* was isolated by treatment of the solution with water and dilute sulphuric acid and subsequent removal of the solvent and treated with a slight excess of semicarbazide acetate in aqueous-alcoholic solution. The *semicarbazone*, after crystallising several times from alcohol, melted at  $198^{\circ}$  (Found: C, 58.0; H, 8.8.  $C_{13}H_{23}O_3N_3$  requires C, 58.0; H, 8.6%). When it (36 g.) was heated with 50 c.c. of concentrated hydrochloric acid and 150 c.c. of water on the steam-bath for  $2\frac{1}{2}$  hours, the ester separated as an oil. After cooling, this was taken up in ether, washed with dilute caustic soda solution, dried, and distilled in a vacuum, the *keto-ester* being obtained as a mobile colourless liquid with a characteristic odour, b. p.  $135^{\circ}/11$  mm.,  $d_4^{17}$  1.04555,  $n_D^{17}$  1.4733 (whence  $[R_L]_D = 56.91$ . Calc., 57.08),  $[\alpha]_D^{25} + 21.3^{\circ}$  in 2.2% alcoholic solution (Found: 67.9; H, 9.6.  $C_{12}H_{20}O_3$  requires C, 67.9; H, 9.4%).

The same semicarbazone was obtained from the *keto-ester* produced from *allo-methyl hydrogen camphorate* by a similar series of reactions.

*Hydrolysis of the Keto-ester (VI). Preparation of the Keto-acid (XIV) and the Hydroxy-lactone (XVIII).*—The *keto-ester* (14 g., purified through the semicarbazone) was heated with aqueous-alcoholic potassium hydroxide (16 g.) on the steam-bath for 18–20 hours, the alcohol evaporated, the residue diluted with water and extracted with ether to remove any unchanged ester, and the alkaline solution acidified with hydrochloric acid. After a day or two, the oil that had separated partly solidified. The solid was drained on porous plate and crystallised from petroleum (b. p.  $60$ – $80^{\circ}$ ). Feathery needles of the *diketo-compound* (XVII) described below separated first, and then the *keto-acid* (XIV) in well-formed rhombic plates, m. p.  $96^{\circ}$  after two recrystallisations (Found: C, 66.7; H, 9.3; *M*, by titration, 197.  $C_{11}H_{18}O_3$  requires C, 66.7; H, 9.1%; *M*, 198).

*5-Acetyl-1:1:2-trimethylcyclopentane-2-carboxylic acid* is very soluble in the ordinary organic solvents except light petroleum. It has  $[\alpha]_D^{25} + 99.1^{\circ}$  in about 2.3% solution in chloroform. The *semicarbazone* (XVI), crystallised from methyl alcohol, melts at  $225^{\circ}$  (Found: C, 56.8; H, 8.5.  $C_{12}H_{21}O_3N_3$  requires C, 56.5; H, 8.2%).

The oil absorbed in the porous plate (above) was extracted with ether, dried, and distilled in a vacuum; the somewhat viscous mass

obtained, b. p. 186—187°/14 mm., showed no tendency to solidify (Found: C, 66.8; H, 9.1%). The oil was slowly attacked by dilute sodium bicarbonate solution. After treatment with semicarbazide acetate in dilute methyl alcohol, it gave on dilution a gummy mass which gradually solidified: by slow evaporation of a solution of the solid in hot dilute methyl alcohol, a substance of indefinite crystalline structure was obtained. This was dried in the air, washed with benzene to remove a small quantity of colouring matter, and dried over sulphuric acid in a vacuum desiccator; it then melted at 172° and decomposed at a higher temperature. The substance (? XIX) is isomeric with the semicarbazone (XVI) (Found: C, 56.8; H, 8.3%). It dissolves slowly in dilute sodium hydroxide solution and is recovered on acidification.

*Behaviour of the Keto-acid (XIV) and the Hydroxy-lactone (XVIII) towards Acetyl Chloride.*—Either of the acids (3 g.) was heated with excess of acetyl chloride (8 c.c.) on the steam-bath for a few hours, the acetyl chloride then evaporated, and the residue treated with water; the oil produced was dissolved in ether and shaken with dilute sodium carbonate solution. The neutral product gave only a trace of the unsaturated lactone described below. The alkaline extract on acidification gave an acid, which crystallised from hot water in shimmering plates, m. p. 73°; after being dried in the air for a day, it was analysed (Found: C, 60.9; H, 9.5; *M*, by titration, 215.5.  $C_{11}H_{20}O_4$  requires C, 61.1; H, 9.3%; *M*, 216). The acid is the hydrated form (XX) of the keto-acid (XIV) and is converted into this acid on being dried in a desiccator.

*Action of Acetic Anhydride on the Keto-acid (XIV) and the Hydroxy-lactone (XVIII).*—Either compound (5 g.) was refluxed with acetic anhydride (5 c.c.) for 2 hours, and the product distilled; the unsaturated lactone (XXI) passed over at 136°/22 mm. and solidified in the receiver. The lactone, m. p. 62°,  $[\alpha]_D^{25} + 77.7^\circ$  in a 3.3% solution in chloroform (Found: C, 73.1; H, 8.9.  $C_{11}H_{16}O_3$  requires C, 73.3; H, 8.8%), is extremely soluble in almost all organic solvents. It absorbs bromine very readily in chloroform solution.

*Methylcampholide (XXII).*—To a boiling solution of the keto-acid (XIV) (4.5 g.) in absolute alcohol (20 c.c.), sodium (5 g.) was added, followed by 75 c.c. of alcohol in three instalments during 2 hours' additional heating. The alcohol was evaporated on the steam-bath, and the residue diluted with water and acidified with concentrated hydrochloric acid. The oil obtained crystallised after the usual treatment with ether and dilute sodium carbonate solution. *Methylcampholide*, recrystallised from petroleum (b. p. 60—80°), melted at 100—101° (Found: C, 72.3; H, 9.9.  $C_{11}H_{18}O_2$  re-



quires C, 72.5; H, 9.8%) and had  $[\alpha]_D^{25} - 44.8^\circ$  in about 2.02% solution in chloroform.

1 : 8 : 8-*Trimethylbicyclo*[1 : 2 : 3]*octane-2 : 4-dione* (XVII).—The keto-ester (VI) (21 g.) was heated with alcoholic sodium ethoxide (sodium, 2.5 g.; alcohol, 55 c.c.) for 48 hours, the alcohol evaporated, and the residue diluted, extracted with ether, and acidified with concentrated hydrochloric acid. The oil obtained, which solidified, was dried and crystallised from petroleum, separating in slender short needles, m. p.  $220^\circ$  to a red liquid (Found: C, 73.2; H, 9.1.  $C_{11}H_{16}O_2$  requires C, 73.3; H, 8.8%). The *diketo*-compound was optically inactive, dissolved in dilute alkali solutions, gave a brown coloration with alcoholic ferric chloride, and absorbed bromine in chloroform with evolution of hydrogen bromide.

*Homoepicamphor* (XXIII) and the *Keto-alcohol* (XXV).—The compound (XVII) (5 g.) was heated under reflux with amalgamated zinc (25 g.), concentrated hydrochloric acid (100 c.c.), and water (50 c.c.); the reduction product partly distilled into the condenser. After cooling, the product was extracted with ether, the unchanged *diketo*-compound removed by dilute alkali solution, the ethereal solution dried, and the solvent removed. The residue was treated with semicarbazide acetate in methyl-alcoholic solution, and the mixture diluted with water and shaken with light petroleum. The residual *semicarbazone*, after crystallising from dilute methyl alcohol, melted at  $220^\circ$  (Found: C, 64.5; H, 9.8.  $C_{12}H_{21}ON_3$  requires C, 64.5; H, 9.4%). The quantity of it was very small and the ketone could not be regenerated. The petroleum solution gave a small quantity of a semi-solid substance which was probably the keto-alcohol (XXV).

The author wishes to express his grateful thanks to Professor J. F. Thorpe, C.B.E., F.R.S., for his interest in this work and for his many valuable suggestions, and to the Government of Bengal, India, for a foreign scholarship and a grant towards the purchase of chemicals.

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### XXX.—*The cis-trans Ethenoid Transformation.*

By GEORGE ROGER CLEMO and STANLEY BROWN GRAHAM.

THE mechanism of the stereoisomeric transformation of ethylenic compounds has received considerable attention but remains far from clear. Several early workers noted that maleic acid and its

esters were converted into the fumaric form by minerals acids, and Tanatar (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1742) and Pfeiffer (*Ber.*, 1914, **47**, 1592) describe the change of maleic to fumaric acid by means of ammonia and pyridine respectively. Recently, Meerwein and Weber (*Ber.*, 1925, **58**, 1266) have stated that potassium in ether converts methyl maleate into methyl fumarate.

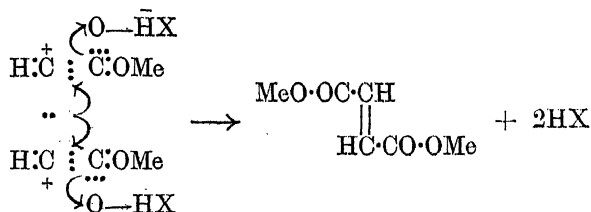
As methyl fumarate is a highly crystalline solid with a solubility of about 1% in methyl maleate at the ordinary temperature, the conversion of the latter into the former furnishes a convenient method for studying this reaction.

Apparently, the catalytic action of ammonia and organic bases has not been investigated in this connexion, but it has now been found that the former, and primary and secondary amines, effect the change. For instance, a trace of piperidine transforms methyl maleate in a few seconds into a crystalline mass of the fumarate, and since the former has much the greater energy content, the temperature rises very considerably. Dimethylamine, diethylamine, piperazine, methylamine, allylamine, benzylamine, *d*- and *l*- $\alpha$ -phenylethylamine,  $\beta$ -phenylethylamine, coniine, and aniline also effect the change, although some of them do not bring about a complete transformation. Tertiary amines such as triethylamine, dimethylaniline, diethylaniline, and pyridine, however, do not catalyse the inversion, although triethylamine is a much stronger base than many of the above primary and secondary ones. At first it seemed that triethylamine was an exception to the rule, as the base supplied by Kahlbaum effected some change; but after it had been freed from primary and secondary impurities by treatment with toluene-*p*-sulphonyl chloride (Clemo and Perkin, *J.*, 1921, **119**, 648), it caused no conversion after a year at the ordinary temperature.

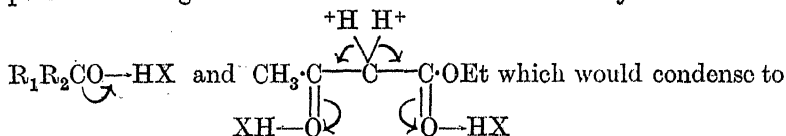
The mechanism usually favoured for the ethenoid inversion is that the catalyst adds itself in some way to the double bond, thus allowing free rotation with formation of the *trans*-form and regeneration of the catalyst. Even if it is assumed that a newly formed molecule may have enhanced activity, there still appears to be no adequate reason why some of the additive complexes should not reach a stable maturity.

Our experiments have shown that organic bases are only effective as catalysts when they contain amino- or imino-hydrogen, and this suggested the following mechanism for the inversion, in which the first stage is the formation of a co-ordinate link between the hydrogen atom of the base and the carbonyl oxygens of the ester. This would produce a mobility in the, at present, uncertain electronic system constituting the double bond, and lead to a very unstable complex

in which both the ethylenic carbon atoms would become positive and surrounded by only seven electrons.



The well-known catalytic action of primary and secondary bases in the Knoevenagel reaction (*Annalen*, 1894, **281**, 25) may be explained as being due to the formation of two ionised systems such as



give the reaction products.

Walden (*Z. physikal. Chem.*, 1896, **20**, 379) states that methyl maleate can be made from either maleic acid or anhydride, but no details are given, and recent workers have used the silver salt-methyl iodide method of preparation. It has now been found that methyl maleate can be easily prepared in good yield from maleic anhydride, methyl alcohol, and sulphuric acid.

#### EXPERIMENTAL.

*Methyl Maleate*.—Maleic anhydride (60 g.) was added to methyl alcohol (100 c.c.) and concentrated sulphuric acid (4 c.c.), and the mixture refluxed for 3½ hours on the water-bath. The bulk of the excess of alcohol was then distilled off and water added, followed by solid sodium carbonate to neutralise the sulphuric acid. The ester, when extracted with ether, dried over sodium sulphate, and fractionated, gave (a) 6 g., b. p. 200–204°, (b) 65 g., b. p. 204–206°, and (c) 1–2 g., b. p. above 206°. Fraction (a) alone contained traces of methyl fumarate, as shown by the silver nitrate test after hydrolysis with baryta [Found for (b): C, 49.7; H, 5.4. Calc. for C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>: C, 50.0; H, 5.55%].

The methyl fumarate formed by the inversion of the above was identified by the method of mixed m. p. with an authentic specimen.

XXXI.—*The Methylation of the Oximes of Benzil.*  
*Part II. The Monomethyl Ethers of the Benzildioximes.\**

By OSCAR L. BRADY and MORRIS MARCUS MUERS.

THE preparation of the monomethyl ethers of the benzildioximes was undertaken with a view to the study of their metallic complexes, which will be described in a subsequent paper. In addition it was hoped that it might be possible to prepare, through these compounds, the hitherto unknown dimethyl ethers of  $\gamma$ -benzildioxime and the *NN*-dimethyl- $\beta$ -benzildioxime (Brady and Perry, J., 1925, 127, 2874).

*O*-Methyl- $\alpha$ -benzilmonoxime (I) on oximation gives a mixture of *O*-monomethyl- $\alpha$ -benzildioxime (II) and  $\alpha'$ -*O*-monomethyl- $\gamma$ -benzildioxime (III). (The symbols  $\alpha'$  and  $\beta'$  are used to indicate the oximino-group methylated in the  $\gamma$ -dioxime,  $\alpha'$  being applied when the methylated hydroxyl group is vicinal and  $\beta'$  when it is remote from the phenyl group.)

$\alpha$ -Benzildioxime (IV) on monomethylation gives a mixture of the former compound (II) and *N*-monomethyl- $\alpha$ -benzildioxime (V). *O*-Monomethyl- $\alpha$ -benzildioxime (II) on further methylation yields *OO*-dimethyl- $\alpha$ -benzildioxime (VI) and *ON*-dimethyl- $\alpha$ -benzildioxime (VII).  $\alpha'$ -Monomethyl- $\gamma$ -benzildioxime (III) on further methylation gives *OO*-dimethyl- $\alpha$ -benzildioxime (VI) and *OO*-dimethyl- $\gamma$ -benzildioxime (VIII), and *N*-monomethyl- $\alpha$ -benzildioxime (V) yields *ON*-dimethyl- $\alpha$ -benzildioxime (VII) and *NN*-dimethyl- $\alpha$ -benzildioxime (IX).

The dimethyl ethers of  $\alpha$ -benzildioxime, described in Part I (Brady and Perry, *loc. cit.*), establish the configuration of the monomethyl ethers from which they can be prepared. *O*- and *N*-Ethers were distinguished by heating with hydriodic acid, methyl iodide and methylamine, respectively, being obtained. The configuration of  $\alpha'$ -*O*-monomethyl- $\gamma$ -benzildioxime will be discussed later.

*O*-Monomethyl- $\alpha$ -benzildioxime (II) was converted by boiling with aniline for 30 seconds into  $\alpha'$ -*O*-monomethyl- $\gamma$ -benzildioxime (III), the change being analogous to that of  $\alpha$ -benzildioxime to  $\beta$ -benzildioxime under similar conditions (J., 1925, 127, 2880); in the present case, however, brief treatment caused isomerisation of the unmethylated group only; more prolonged boiling with aniline or with hydrogen chloride in glacial acetic acid resulted in isomerisation of the methylated group also, giving *O*-monomethyl- $\beta$ -benzildioxime (XII).

\* The new configurations of Meisenheimer (*Ber.*, 1921, 54, 3206) are used throughout this paper.



*O*-Methyl- $\beta$ -benzilmonoxime (XI) does not react readily with hydroxylamine, it being necessary to heat it to 175–185° with hydroxylamine hydrochloride in alcohol; *O*-monomethyl- $\beta$ -benzildioxime (XII) is then formed exclusively. If any of the  $\beta'$ -*O*-monomethyl- $\gamma$ -benzildioxime (XVI) were formed, it would certainly undergo isomeric change under these conditions. The dichloride  $\text{PhC}(\text{NOMe})\cdot\text{CCl}_2\text{Ph}$ , which might react more readily, could not be prepared, since phosphorus pentachloride was without action on *O*-methyl- $\beta$ -benzilmonoxime.

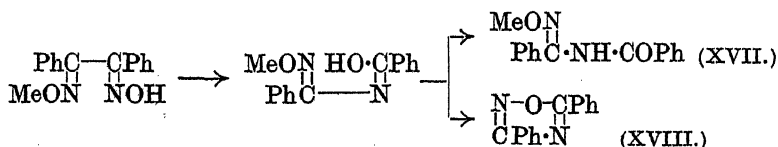
The monomethylation of  $\beta$ -benzildioxime (X) leads to the formation of *O*-monomethyl- $\beta$ -benzildioxime (XII) and *N*-monomethyl- $\beta$ -benzildioxime (XIII). *O*-Monomethyl- $\beta$ -benzildioxime on further methylation gave *ON*- and *OO*-dimethyl- $\beta$ -benzildioxime (XIV and XV), and *N*-monomethyl- $\beta$ -benzildioxime gave *O*-methyl- $\beta$ -benzilmonoxime (XI), formed probably by the hydrolysis of *ON*-dimethyl- $\beta$ -benzildioxime.

From the monomethylation of  $\gamma$ -benzildioxime (XXII), only *N*-monomethyl- $\beta$ -benzildioxime (XIII) could be isolated, isomeric change occurring. From the other liquid products of the reaction, no *O*- or *N*-monomethyl- $\gamma$ -benzildioximes could be isolated.

When *N*-monomethyl- $\alpha$ -benzildioxime was boiled with aniline, the *N*-methyloximino-group was eliminated and replaced by the anil group, but if dimethylaniline was used, isomerisation occurred and *N*-monomethyl- $\beta$ -benzildioxime was formed: this is the first example of such isomerisation of an *N*-ether.

The results so far described are summarised in the diagram.

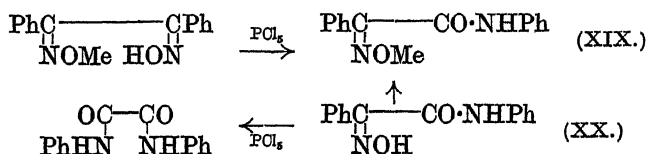
Unlike the *OO*-dimethyl ethers, the *O*-monomethyl ethers undergo the Beckmann rearrangement. *O*-Monomethyl- $\alpha$ -benzildioxime gives *N*-benzoyl-*O*-methylbenzamidoxime (XVII) at 0° and 3:5-diphenyl-1:2:4-oxadiazole (XVIII) at room temperature, methyl alcohol being eliminated in the latter case.



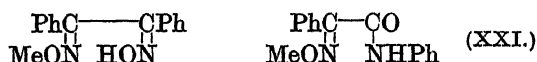
At room temperature, either the phosphorus pentachloride causes the isomerisation of the methylated oximino-group or *trans*-ring formation must take place; in the latter case, the usual explanation of salt formation between the two groups seems inadmissible,

$\begin{array}{c} \text{MeO} \cdot \text{NH} \cdot \text{O} \cdot \text{CPh} \\ \text{PhC} \text{---} \text{N} \end{array}$ , since *O*-methyl ethers are destitute of basic properties.

*O*-Monomethyl- $\beta$ -benzildioxime in the Beckmann rearrangement gives  $\beta$ -*O*-methylphenylglyoxyylanilideoxime (XIX), which has been synthesised by the methylation of phenylglyoxyylanilideoxime (XX), whose orientation is known by its conversion into oxanilide in the Beckmann rearrangement.



$\alpha'$ -*O*-Monomethyl- $\gamma$ -benzildioxime undergoes the Beckmann rearrangement with the formation of  $\alpha$ -*O*-methylphenylglyoxyylanilideoxime (XXI).



It has not been possible to synthesise this compound, but the production of aniline by hydrolysis fixes the relative positions of hydroxyl and phenyl in the oximino-group and the formation of  $\beta$ -*O*-methylphenylglyoxyylanilideoxime (XIX) from *O*-monomethyl- $\beta$ -benzildioxime eliminates the possibility of the methoxyl group being on the opposite side of the nitrogen atom in  $\alpha'$ -*O*-monomethyl- $\gamma$ -benzildioxime. Moreover,  $\beta$ -*O*-methylphenylglyoxyylanilideoxime (XIX) is readily converted by boiling concentrated hydrochloric acid (a reagent which commonly causes isomerisation of an NOME group) into the  $\alpha$ -isomeride (XXI).

#### EXPERIMENTAL.

*O*-Methyl- $\alpha$ -benzilmonoxime.— $\alpha$ -Benzilmonoxime was prepared by a modification of the method of Auwers and Meyer (*Ber.*, 1889, 22, 540). A suspension of benzil (200 g.) in alcohol (700 c.c.), obtained by rapid cooling of the boiling solution, was cooled to 10° and treated below 15° with alternate small quantities of sodium hydroxide (100 g. in 100 c.c. of water) and hydroxylamine hydrochloride (66 g. in 100 c.c. of water). After being kept for 24 hours at room temperature, the mixture was diluted to 4 litres, a small quantity of benzil removed, and the oxime precipitated with concentrated hydrochloric acid or saturated ammonium chloride solution. The washed and dried precipitate was crystallised from benzene, which gave a much better separation of the  $\alpha$ - and  $\beta$ -benzilmonoximes than the 30% alcohol used by Auwers and Meyer. Yield, 70%. The oxime was converted into *O*-methyl- $\alpha$ -benzilmonoxime by the method of Brady and Perry (*loc. cit.*).

*Oximation of O-Methyl- $\alpha$ -benzilmonoxime.*—Finely divided *O*-methyl- $\alpha$ -benzilmonoxime (20 g.) was suspended in alcohol (60 c.c.) and sodium hydroxide (8 g.) and hydroxylamine hydrochloride (7 g.), each dissolved in 8 c.c. of water, were added in small portions. The mixture became hot and the *O*-methyl- $\alpha$ -benzilmonoxime dissolved to give a dark yellow solution. After 2 hours, small crystals filled the liquid, and on the next day these were collected and washed with a little alcohol (A). The filtrate when diluted to 200 c.c. gave a crystalline precipitate (B) and saturation of the mother-liquor with carbon dioxide gave a further precipitate (C).

The precipitate A, consisting of a sparingly soluble sodium salt, was dissolved in hot 2*N*-sodium hydroxide, some unchanged *O*-methyl- $\alpha$ -benzilmonoxime removed, and the solution cooled and saturated with carbon dioxide; the precipitate, after crystallising three times from acetone, gave *O*-monomethyl- $\alpha$ -benzildioxime (II) in flat needles, m. p. 181—182° (Found: N, 11.4; OMe, 9.2.  $C_{15}H_{14}O_2N_2$  requires N, 11.0; OMe, 12.2%). Low methoxyl values are usual with compounds of this type (compare Brady and Perry, *loc. cit.*).

When the above compound was boiled for 15 minutes with acetic anhydride, the mixture treated with water, and the product crystallised from alcohol, *acetyl-O*-monomethyl- $\alpha$ -benzildioxime was obtained in small plates, m. p. 107—108° (Found: N, 9.5.  $C_{17}H_{16}O_3N_2$  requires N, 9.4%). *Benzoyl-O*-monomethyl- $\alpha$ -benzildioxime, prepared by the Schotten-Baumann reaction, crystallised from glacial acetic acid in needles, m. p. 167° (Found: N, 7.8.  $C_{22}H_{18}O_3N_2$  requires N, 7.7%).

Fractions B and C when crystallised from various solvents gave a product, m. p. 157—160°, which was seen under the microscope to consist of approximately equal quantities of flat needles and small octahedra. When the mixture was dissolved in hot 2*N*-sodium hydroxide, and the solution cooled, the sodium salt of most of the *O*-monomethyl- $\alpha$ -benzildioxime separated; the mother-liquor, on saturation with carbon dioxide, gave a pasty solid which soon set to a brittle mass. Two crystallisations of this from glacial acetic acid gave a product, m. p. 165—167°: in later preparations, the separation was greatly assisted by seeding the acetic acid solution with these crystals and filtering the liquid before crystallisation was complete, whereby the bulk of the new compound was removed before the *O*-monomethyl- $\alpha$ -benzildioxime separated. Further crystallisation from acetic acid did not increase the purity of the product, as this treatment brought about partial conversion into a third isomeride, but crystallisation from chloroform and light



petroleum gave  $\alpha'$ -O-monomethyl- $\gamma$ -benzildioxime (III) in small octahedra, m. p.  $172^\circ$  (Found: N, 10.9; OMe, 9.6%).

*Acetyl- $\alpha'$ -O-monomethyl- $\gamma$ -benzildioxime* crystallised from alcohol in needles, m. p.  $80^\circ$  (Found: N, 9.6%), and *benzoyl- $\alpha'$ -O-monomethyl- $\gamma$ -benzildioxime* from glacial acetic acid in prisms, m. p.  $79^\circ$  (Found: N, 7.9%). Both compounds were prepared by the methods described above.

In the above oximation the final yields averaged 40–50% of the  $\alpha$ - and 7–10% of the  $\gamma$ -benzildioxime derivative with about 25% of inseparable mixture. Many unsuccessful attempts were made to obtain larger yields of  $\alpha'$ -O-monomethyl- $\gamma$ -benzildioxime: oximation in hot solution with free hydroxylamine gave but a small yield of the mixture; in hot acid solution, or with hydroxylamine hydrochloride alone in alcohol, much of the product was converted into O-monomethyl- $\beta$ -benzildioxime; in alkaline solution as above but at a higher temperature, much hydroxylamine was destroyed and a poor yield of the mixture obtained.

*Oximation of O-Methyl- $\beta$ -benzilmonoxime.*—O-Methyl- $\beta$ -benzilmonoxime, prepared by boiling O-methyl- $\alpha$ -benzilmonoxime with concentrated hydrochloric acid (Brady and Perry, *loc. cit.*), is unaffected by treatment with hydroxylamine in acid, alkaline, or neutral solution even at  $100^\circ$ . When, however, the compound (5 g.) was heated under pressure with hydroxylamine hydrochloride (1.8 g.) in alcohol (25 c.c.) at  $175$ – $185^\circ$  for 10 hours, and the solution cooled, a solid separated on scratching which, after crystallising three times from glacial acetic acid, gave O-monomethyl- $\beta$ -benzildioxime (XII) in stout prisms, m. p.  $177^\circ$  (Found: N, 11.1; OMe, 10.9%).

Mixtures of any two of the isomeric monomethylbenzildioximes obtained melted between  $130^\circ$  and  $150^\circ$ .

*Acetyl-O-monomethyl- $\beta$ -benzildioxime* crystallised from alcohol in prisms, m. p.  $81^\circ$  (Found: N, 9.5%), and *benzoyl-O-monomethyl- $\beta$ -benzildioxime* from glacial acetic acid in prisms, m. p.  $162^\circ$  (Found: N, 7.8%).

In this oximation no indication of  $\beta'$ -O-monomethyl- $\gamma$ -benzildioxime was obtained. This result was, however, to be expected owing to the instability of the derivatives of  $\gamma$ -benzildioxime, which at high temperatures change to the  $\beta$ -isomerides.

*Monomethylation of  $\alpha$ -Benzildioxime.*—A solution of  $\alpha$ -benzildioxime (10 g.) in 4*N*-sodium hydroxide (200 c.c.) and methyl alcohol (5 c.c.) was cooled in ice, and methyl sulphate (15 g.) added slowly. The precipitate which formed was collected, washed with cold 2*N*-sodium hydroxide, and extracted with hot *N*/5-sodium hydroxide; a small quantity of oil remained consisting of dimethyl

ethers. The alkaline extract on saturation with carbon dioxide gave *O*-monomethyl- $\alpha$ -benzildioxime. The mother-liquor from the methylation was saturated with carbon dioxide, the precipitate obtained was extracted with hot alcohol, some undissolved  $\alpha$ -benzildioxime removed, and the solid which separated on cooling was crystallised from alcohol, *N*-monomethyl- $\alpha$ -benzildioxime (V) being obtained in prisms, m. p.  $168^{\circ}$  (Found: N, 11.4.  $C_{15}H_{14}O_2N_2$  requires N, 11.0%). This compound gave no methyl iodide on treatment with hydriodic acid, but methylamine was detected in the solution by Valton's method (J., 1925, 127, 40).

*Monomethylation of  $\beta$ -Benzildioxime.*—This was carried out in the same way as that of  $\alpha$ -benzildioxime. The pasty precipitate of dimethyl ethers was removed and the filtrate diluted and saturated with carbon dioxide; the semi-solid precipitate obtained slowly hardened and after three crystallisations from alcohol gave a small yield of *O*-monomethyl- $\beta$ -benzildioxime. The mother-liquors from the crystallisation were evaporated to dryness at room temperature and the residue was extracted several times with boiling light petroleum and once with hot benzene, a further quantity of the *O*-methyl ether thus being removed; the undissolved part, crystallised from alcohol, gave *N*-monomethyl- $\beta$ -benzildioxime (XIII) in hexagonal prisms, m. p.  $205^{\circ}$  (decomp.) (Found: N, 11.2%). Hydriodic acid produced no methyl iodide from this compound, but methylamine was detected.

*Monomethylation of  $\gamma$ -Benzildioxime.*—The dioxime (5 g.) was dissolved in 2*N*-sodium hydroxide (100 c.c.), and a concentrated solution of sodium hydroxide (7 g.) added with cooling, followed by a little methyl alcohol (2.5 c.c.); the suspension of sodium salt obtained was cooled in ice, and methyl sulphate (4 g.) added. After 30 minutes, the mixture was diluted until solution was attained and an excess of a saturated solution of ammonium chloride was then added. The precipitate obtained, on crystallising twice from alcohol, gave *N*-monomethyl- $\beta$ -benzildioxime (2 g.). The mother-liquors from the crystallisation were evaporated at room temperature and the residue was extracted with hot benzene; some *N*-ether remained undissolved. The benzene solution on evaporation yielded a considerable quantity of oil, but no pure compound could be obtained therefrom.

*Methylation of *O*-Monomethyl- $\alpha$ -benzildioxime.*—A solution of the compound (5 g.) in hot 2*N*-sodium hydroxide (120 c.c.) was quickly cooled and methyl alcohol (5 c.c.) added, followed by methyl sulphate (10 g.) in small portions with cooling in ice. After some hours, the pasty solid was collected and crystallised first from glacial acetic acid and then from acetone; the *OO*-dimethyl- $\alpha$ -benzil-

dioxime obtained was identified by comparison with a specimen prepared by Brady and Perry's method. When the acetic acid mother-liquor was diluted somewhat with water, more of the above compound separated; this was removed, excess of water added to the filtrate, the precipitate formed dissolved in the minimum quantity of glacial acetic acid, and concentrated hydrochloric acid added until no further precipitate was formed. The precipitated hydrochloride (m. p. 157—161°) was washed with concentrated hydrochloric acid, then with hot benzene, and decomposed with concentrated aqueous ammonia. The solid obtained, after crystallisation from alcohol, was identified as *ON*-dimethyl- $\alpha$ -benzil-dioxime.

*Methylation of N-Monomethyl- $\alpha$ -benzildioxime.*—The compound (1 g.) was dissolved in 2*N*-sodium hydroxide, the solution cooled in ice, and methyl sulphate (2 g.) added. The oil formed slowly solidified; when it was crystallised from alcohol, *NN*-dimethyl- $\alpha$ -benzildioxime separated. The alcoholic mother-liquor was concentrated somewhat, a further quantity of the *NN*-ether removed, and concentrated hydrochloric acid added to the filtrate; the precipitated hydrochloride, after being washed with concentrated hydrochloric acid and with ether, was decomposed with ammonia, and the solid crystallised from alcohol, *ON*-dimethyl- $\alpha$ -benzil-dioxime being obtained.

*Methylation of O-Monomethyl- $\beta$ -benzildioxime.*—A solution of the compound (5 g.) in hot 2*N*-sodium hydroxide (120 c.c.) was cooled and treated with methyl sulphate (10 g.). The pasty precipitate was extracted with ether, and the solution dried with anhydrous sodium sulphate and saturated with dry hydrogen chloride. The oily hydrochloride precipitated was separated by decantation, united with a further quantity obtained by addition of light petroleum to the ethereal solution, and decomposed with concentrated aqueous ammonia. The oil obtained, after being kept in a vacuum over solid sodium hydroxide, solidified and then, on crystallising several times from light petroleum, gave *ON*-dimethyl- $\beta$ -benzildioxime. The ether-light petroleum solution from which the hydrochloride had been removed was evaporated, and the residue crystallised twice from alcohol, *OO*-dimethyl- $\beta$ -benzil-dioxime being obtained.

*Methylation of  $\alpha'$ -O-Monomethyl- $\gamma$ -benzildioxime.*—A mixture of the compound (2 g.), methyl iodide (1.5 g.), dry ether (20 c.c.), and dry silver oxide (2 g.) was boiled under reflux for 3 hours, cooled, and the liquid filtered. The solid was extracted with hot acetone; the extract on evaporation yielded *OO*-dimethyl- $\alpha$ -benzildioxime. The ethereal solution was evaporated at room temperature, and the

residue crystallised from acetone, a further quantity of the *OO*-ether being obtained. The acetone mother-liquor on evaporation at room temperature gave an oil which solidified when kept in an evacuated desiccator and scratched; crystallised from dilute alcohol and finally from 80% alcohol, this yielded *OO*-dimethyl- $\gamma$ -benzildioxime (VIII) in plates, m. p. 59° (Found: N, 10.3; OMe, 18.1.  $C_{16}H_{16}O_2N_2$  requires N, 10.4; OMe, 23.1%). The melting point of this compound was depressed by 30–40° by addition of an approximately equal quantity of *O*-methyl- $\alpha$ - or - $\beta$ -benzilmonoxime or *OO*-dimethyl- $\beta$ -benzildioxime, m. p.'s 61°, 62°, and 73° respectively.

Methylation of  $\alpha'$ -*O*-monomethyl- $\gamma$ -benzilmonoxime with methyl sulphate as described for *O*-monomethyl- $\alpha$ -benzildioxime gave an oil which did not solidify after several months. When, however, the above compound had been obtained and was used to seed this oil, crystallisation occurred, and recrystallisation from alcohol gave a fair yield of *OO*-dimethyl- $\gamma$ -benzildioxime but no *OO*-dimethyl- $\alpha$ -benzildioxime.

*Isomeric Changes of the Methyl Ethers of the Benzildioximes.*—*O*-Monomethyl- $\alpha$ -benzildioxime (20 g.) was added to boiling, freshly distilled aniline (40 c.c.) and the mixture was boiled for 30 seconds and poured at once into ice-cold dilute hydrochloric acid. The precipitated mixture of the monomethyl ethers of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -benzildioximes, after being thoroughly washed with dilute hydrochloric acid, was separated by removal of unchanged *O*-monomethyl- $\alpha$ -benzildioxime as its sparingly soluble sodium salt and crystallisation of the remaining mixture from acetic acid and from chloroform and light petroleum (p. 220). About 5 g. of  $\alpha'$ -*O*-monomethyl- $\gamma$ -benzildioxime were obtained (this is the easiest way of preparing this compound in quantity). If the time of contact with boiling aniline exceeds 30 seconds, a larger quantity of *O*-monomethyl- $\beta$ -benzildioxime is formed which is very difficult to separate. When *O*-monomethyl- $\alpha$ -benzildioxime (4 g.) was boiled for 5 minutes with aniline (10 c.c.) and cooled, a mass of crystals separated which gave 2 g. of *O*-monomethyl- $\beta$ -benzildioxime after being washed with dilute acid and crystallised from glacial acetic acid.

A suspension of *O*-monomethyl- $\alpha$ -benzildioxime (8 g.) in glacial acetic acid (30 c.c.) was saturated with dry hydrogen chloride and the mixture was boiled under reflux for 30 minutes, cooled and poured into water. The solid obtained, on crystallising from glacial acetic acid, gave 5 g. of *O*-monomethyl- $\beta$ -benzildioxime. Similarly  $\alpha'$ -*O*-monomethyl- $\gamma$ -benzildioxime gave *O*-monomethyl- $\beta$ -benzildioxime.

*OO*-Dimethyl- $\gamma$ -benzildioxime was boiled under reflux with con-

centrated hydrochloric acid for an hour and the solution was diluted with water and extracted with ether; the product, crystallised from acetone, gave *OO*-dimethyl- $\alpha$ -benzildioxime.

*N*-Monomethyl- $\alpha$ -benzildioxime (1 g.) was added to boiling aniline (3 g.) and boiled for 5 minutes. The solution was poured into cold dilute hydrochloric acid, and the resulting precipitate crystallised from alcohol; benzilmonoxime anil,  $\text{CPh}(\text{NOH})\cdot\text{CPh}\cdot\text{NPh}$ , thus obtained was identified by comparison with a specimen prepared by Auwers and Siegfeld's method (*Ber.*, 1893, 26, 794). The readily hydrolysable  $\text{NMe}\cdot\text{O}$  group was eliminated by this treatment, but when dimethylaniline was substituted for aniline *N*-monomethyl- $\beta$ -benzildioxime was obtained.

*Beckmann Rearrangement of O-Monomethyl- $\alpha$ -benzildioxime.*—The compound (5 g.) was suspended in dry ether (20 c.c.) cooled in ice, and phosphorus pentachloride (4 g.) added. After 8 hours' keeping at room temperature, all the oxime had dissolved; the ether was then decanted, washed with ice-cold water, and dried over potassium carbonate; on evaporation an oil was obtained which slowly solidified in a vacuum. The solid, crystallised twice from alcohol, gave 3 : 5-diphenyl-1 : 2 : 4-oxadiazole, identified by comparison with a specimen prepared by Günther's method (*Annalen*, 1889, 252, 48). The alcoholic mother-liquors from the crystallisation were diluted with water; the precipitate obtained, on crystallising twice from benzene, gave flat plates of *N*-benzoyl-*O*-methylbenzamidoxime (XVII), m. p.  $151^\circ$  (Found: N, 11.1; OMe, 11.9.  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{N}_2$  requires N, 11.0; OMe, 12.2%). This compound (0.5 g.) was boiled under reflux with 30% sodium hydroxide solution (10 c.c.) for 1 hour: sodium benzoate separated; the alkaline solution, on extraction with ether, removal of the solvent, and crystallisation of the residue from light petroleum, gave *O*-methylbenzamidoxime, identified by comparison with a genuine specimen (Krüger, *Ber.*, 1885, 18, 1053). Hydrolysis of *N*-benzoyl-*O*-methylbenzamidoxime with concentrated hydrochloric acid gave benzamide and benzoic acid.

In later experiments the oxime-ether-phosphorus pentachloride mixture was kept at  $0^\circ$  until the reaction was complete; a larger proportion of *N*-benzoyl-*O*-methylbenzamidoxime was then formed which could be isolated by direct crystallisation from alcohol and benzene.

*Beckmann Rearrangement of  $\alpha'$ -O-Monomethyl- $\gamma$ -benzildioxime.*—The reaction was carried out as above, but the temperature was kept below  $0^\circ$  by means of a freezing mixture. The solid from the ether, after crystallising three times from alcohol, gave  $\alpha$ -*O*-methylphenylglyoxylanilideoxime (XXI) in long needles, m. p.  $118$ — $120^\circ$

(Found: N, 11.2.  $C_{15}H_{14}O_2N_2$  requires N, 11.0%). Hydrolysis of this compound with boiling concentrated hydrochloric acid and extraction with ether gave an oil, from which a solid (m. p. 57–60°) could be isolated, but in too small quantity for further investigation; the hydrochloric acid solution yielded aniline.

*Beckmann Rearrangement of O-Monomethyl-β-benzildioxime.*—The reaction was carried out at 0° as with the α-compound, the ether yielding a solid which, after crystallising twice from alcohol, gave β-O-methylphenylglyoxylanilideoxime (XIX) in needles, m. p. 152° (Found: N, 11.4%). Boiling concentrated hydrochloric acid converted it first into the α-isomeride; prolonged boiling gave results similar to those obtained with the latter compound. The constitution was proved by the following synthesis. A solution of phenylglyoxylanilide (2 g.), prepared from β-benzilmonoxime by the Beckmann rearrangement, in alcohol (15 c.c.) was cooled in ice, and hydroxylamine hydrochloride (0.7 g.) and sodium hydroxide (0.8 g.), each in 1 c.c. of water, were added slowly. After 2 hours, the whole was poured into water and the precipitated solid, after drying, was extracted with hot benzene, which removed a small quantity of benzanilide. The insoluble portion, together with the precipitate obtained by saturating the original alkaline filtrate with carbon dioxide was crystallised from alcohol, giving the β-phenylglyoxylanilideoxime of Beckmann and Köster (*Annalen*, 1893, 274, 9). This oxime (1 g.) was boiled under reflux with methyl iodide (1 g.), dry silver oxide (0.5 g.), and dry ether (15 c.c.) for 2 hours. After filtration and evaporation of the ether the residual solid was crystallised first from alcohol and then from benzene and light petroleum, β-O-methylphenylglyoxylanilideoxime being obtained.

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### XXXII.—The Isomerism of the Oximes. Part XXXVII. Allyl-p-nitrobenzaldoximes, O- and N-Allylhydroxylamines, and Sulphime S-Ethers.

By OSCAR L. BRADY and FRANK HERBERT PEAKIN.

CLAISEN (*Z. angew. Chem.*, 1923, 36, 478; *Annalen*, 1925, 442, 210) has shown that unsaturated alkyl halides, acting upon sodium phenoxide, give O- or C-alkyl derivatives according as the reaction occurs in an ionising or a non-ionising solvent, and that saturated alkyl halides give only O-alkyl derivatives. Now, in the methylation

of aldoximes the formation of *O*- and *N*-methyl derivatives is probably due to an ionic and a non-ionic reaction respectively (Brady and Goldstein, J., 1926, 2403). It seemed likely, therefore, that the use of an unsaturated alkyl halide might give a greater proportion of *N*-ether. The allylation of aldoximes presented special difficulties: the compounds in many cases did not crystallise and there was a tendency for the formation of resinous polymerisation products; *p*-nitrobenzaldoxime, however, gave a crystalline *O*-allyl and *N*-allyl ether. The relative amounts of the two ethers obtained from the  $\alpha$ -oxime did not seem to differ materially from those of the methyl ethers, but a quantitative determination was impracticable, since extensive resinification occurred when attempts were made to hydrolyse the mixture of ethers in order to estimate the *N*-allylhydroxylamine (compare Brady and Goldstein, *loc. cit.*).

*O*-Allylhydroxylamine hydrochloride has been obtained by the hydrolysis of *O*-allylbenzhydroxamic acid, and a solution of *N*-allylhydroxylamine hydrochloride from *N*-allylbenzaldoxime.

Cinnamyl and styryl halides, reacting with aldoximes, gave only resinous products.

The sulphime *S*-ethers,  $R \cdot CH \cdot N \cdot SR'$ , of Zincke and Farr (*Annalen*, 1912, 391, 60, 74) are analogous to the oxime *O*-ethers and an attempt has been made to obtain them in stereoisomeric forms but without success. Only one ether is obtained by the action of *o*-nitrophenylsulphamine,  $NO_2 \cdot C_6H_4 \cdot S \cdot NH_2$ , on benzaldehyde and on *m*-nitrobenzaldehyde and no isomeric change is brought about by the action of ultra-violet light (compare Brady and Klein, J., 1927, 893).

#### EXPERIMENTAL.

*Allylation of  $\alpha$ -p-Nitrobenzaldoxime.*—Sodium (1.4 g.) was dissolved in alcohol (75 c.c.) and  $\alpha$ -*p*-nitrobenzaldoxime (10 g.) added, followed by allyl iodide (10 g.). After being heated under reflux for 3 hours, the mixture was kept over-night; yellow crystals (5 g.) then separated. Recrystallised from dilute alcohol, they gave  $\alpha$ -*O*-allyl-*p*-nitrobenzaldoxime in very pale yellow needles, m. p. 75° (Found: N, 13.7.  $C_{10}H_{10}O_3N_2$  requires N, 13.6%). This compound is volatile in steam, gives no hydrochloride, and, like other *O*-ethers, is very difficult to hydrolyse.

The mother-liquor from the above preparation was diluted with water; the brown solid precipitated (5 g.), on repeated crystallisation, gave more of the *O*-allyl ether. Concentration of the aqueous mother-liquor, followed by extraction with chloroform, gave a substance (1 g.) which after two crystallisations from benzene and light petroleum was found to be *N*-allyl-*p*-nitrobenzaldoxime, identical with the compound obtained from the  $\beta$ -oxime.

*Allylation of  $\beta$ -p-Nitrobenzaldoxime.*—If the above method be employed with the  $\beta$ -oxime, resinification occurs.

Sodium (0.7 g.) was dissolved in alcohol (20 c.c.),  $\beta$ -p-nitrobenzaldoxime (1.2 g.) added, the solution cooled to room temperature, and allyl iodide (0.7 c.c.) poured in; after 3 days a yellow crystalline material had separated and the whole was poured into water. The precipitate, after several crystallisations from benzene and light petroleum, gave *N*-allyl-*p*-nitrobenzaldoxime in pale yellow prisms, m. p.  $112^\circ$  (Found: N, 13.8.  $C_{10}H_{10}O_3N_2$  requires N, 13.6%). With dry hydrogen chloride in dry chloroform, this ether gave a slightly gummy, very hygroscopic precipitate of *N*-allyl-*p*-nitrobenzaldoxime hydrochloride, m. p.  $61$ – $64^\circ$  (Found: Cl, 14.1.  $C_{10}H_{10}O_3N_2 \cdot HCl$  requires Cl, 15.0%). The material was prepared for analysis by rapid pressure on porous tile, and the melting-point determination and the analysis were carried out at once.

*O-Allylhydroxylamine Hydrochloride.*—Benzhydroxamic acid (5 g.) in alcohol (16 c.c.) was treated with sodium hydroxide (1.5 g. in the minimum quantity of water) and allyl bromide (4 c.c.) in alcohol (10 c.c.), and the mixture heated under reflux for 30 minutes. The alcohol was removed on the water-bath, water (20 c.c.) added, and the oil extracted with chloroform. After removal of the solvent, cooling, and scratching, the residual oil solidified (5 g.), and crystallisation from benzene and light petroleum gave *O*-allylbenzhydroxamic acid in colourless needles, m. p.  $58^\circ$  (Found: N, 8.0.  $C_{10}H_{11}O_2N$  requires N, 7.9%). This compound (4 g.) was heated under reflux with alcohol (10 c.c.) and concentrated hydrochloric acid (4 c.c.) for 45 minutes; the product was diluted with water and extracted several times with chloroform. Evaporation of the aqueous solution on the water-bath left a deliquescent crystalline mass, which, after being pressed on porous tile and dried in a desiccator, consisted of colourless leaflets of *O*-allylhydroxylamine hydrochloride, m. p.  $172^\circ$  (decomp.) (Found: Cl, 33.6; N, 13.4.  $C_3H_7ON \cdot HCl$  requires Cl, 32.5; N, 12.8%). It had no reducing action on Fehling's solution and on treatment with *p*-nitrobenzaldehyde in alcohol gave  $\alpha$ -*O*-allyl-*p*-nitrobenzaldoxime.

*N-Allylhydroxylamine Hydrochloride.*— $\beta$ -Benzaldoxime (10 g.), suspended in alcohol (20 c.c.), was treated with sodium ethoxide (2 g. of sodium in 50 c.c. of alcohol), and allyl bromide (3 c.c.) added. After 12 hours, the alcohol was removed on the water-bath, water added, the oil extracted with chloroform, and the solvent removed. The crude *N*-ether could not be induced to crystallise, so it was heated under reflux with alcohol (20 c.c.) for 15 minutes, the odour of benzaldehyde soon being perceptible. The solution was evaporated on the water-bath, the aldehyde being carried off in the water



vapour. The semi-solid residue yielded nothing crystalline; in aqueous solution, however, it immediately reduced Fehling's solution in the cold, and on treatment with an alcoholic solution of *p*-nitrobenzaldehyde and aqueous sodium carbonate gave *N*-allyl-*p*-nitrobenzaldoxime.

*Sulphime S-Ethers*.—*o*-Nitrophenylsulphamine (1.4 g.; prepared by the method of Zincke and Farr, *loc. cit.*) in alcohol (25 c.c.) was heated under reflux for 10 minutes with *m*-nitrobenzaldehyde (1.3 g.). The solid which separated on cooling (2 g.), on crystallisation from benzene, gave *m*-nitrobenzylidene-*o*-nitrophenylsulphamine in lemon-yellow needles, m. p. 192° (Found: N, 13.9.  $C_{13}H_9O_4N_3S$  requires N, 13.9%). Examination of the mother-liquors from the preparation and from the crystallisation gave no indication of the presence of an isomeride: a similar result was obtained in the case of benzylidene-*o*-nitrophenylsulphamine (m. p. 161°) prepared by Zincke and Farr's method.

Both benzylidene- and *m*-nitrobenzylidene-*o*-nitrophenylsulphamine were exposed in benzene solution for 48 hours in silica tubes to the light of a quartz-mercury lamp, but were recovered unchanged on removal of the solvent.

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### XXXIII.—*The Parachor and Chemical Constitution.* *Part XIV. Tellurium Compounds.*

By FRANCIS HEREWARD BURSTALL and SAMUEL SUGDEN.

IN earlier papers of this series (Sugden, Reed, and Wilkins, J., 1925, 127, 1525; Henley and Sugden, J., 1929, 1058), a number of compounds of sulphur and selenium have been examined in which these elements exert a valency which is greater than the normal, *viz.*, 2. In every case the shell of eight electrons around the sulphur or selenium atom is not exceeded, and the parachors show the presence of the correct number of semipolar double bonds or singlet linkages which are necessary to maintain the octet. As a result of the work described below, this conclusion can now be extended to tellurium compounds. We have so far not found any telluroxides or other compounds containing semipolar double bond which are sufficiently stable in the fused state for parachor measurements; the dialkyl- and diaryl-tellurium dihalides are, however, remarkably stable substances, and measurements can be made for a considerable temperature interval above their melting points. In all but one of the substances examined, the parachor anomaly

predicted for the singlet linkages in the molecule has been realised experimentally.

It was necessary in the first place to determine the atomic constant for tellurium by measurements of the parachors of compounds in which this element exerts its normal valency of two. Data for such compounds are given in Table I. The figure recorded for diphenyl telluride is that obtained by Lowry and Gilbert (J., 1929, 2087). The ditelluride (6) began to decompose at its melting point,

TABLE I.  
*Atomic Parachor of Tellurium.*

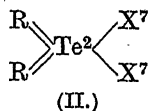
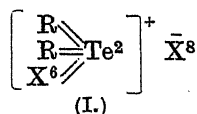
Substance.	Formula.	[P] obs.	$\Sigma[P]$ .	Te.
(1) Diphenyl telluride	$\text{Ph}_2\text{Te}$	457.4	380.0	77.4
(2) Dianisyl telluride	$(\text{MeO}\cdot\text{C}_6\text{H}_4)_2\text{Te}$	575.2	498.0	77.2
(3) <i>Di-n-butyl telluride</i>	$(\text{C}_4\text{H}_9)_2\text{Te}$	426.8	346.2	80.6
(4) Phenoxtellurine*	$\text{C}_6\text{H}_4 < \overset{\text{Te}}{\text{O}} > \text{C}_6\text{H}_4$	452.9	371.9	81.0
(5) Di-2-chloro- <i>p</i> -phenetyl telluride†	$(\text{EtO}\cdot\text{C}_6\text{H}_3\text{Cl})_2\text{Te}$	731.2	650.4	80.8
(6) Di- <i>p</i> -phenetyl ditelluride	$(\text{EtO}\cdot\text{C}_6\text{H}_4)_2\text{Te}_2$	723.0	576.6	(73.2)
		Mean, excluding (6)		79.4

\* The heterocyclic 6-membered ring in this substance is assumed to have the normal value of 6.1 units.

† See p. 231.

so the value given for its parachor can only be regarded as approximate. The mean constant for tellurium, *viz.*, 79.4, is a little lower than the value 86 predicted from the parachors of adjacent elements (Henley and Sugden, *loc. cit.*), but lies satisfactorily between the constants for antimony (66.0) and iodine (91.0). The series, O = 20, S = 48.2, Se = 62.5, Te = 79.4, shows the same steady increase with atomic number which has been observed in other families of elements, *e.g.*, the halogens.

Table II gives the parachors of a number of tellurium compounds in which this element is quadrivalent, the data for compounds (3)—(5) being due to Lowry and Gilbert (*loc. cit.*). These substances are all of the type  $\text{R}_2\text{TeX}_2$ , where X is a halogen atom, and may be formulated electronically as salts (I) or as non-polar compounds (II); their properties, excepting those of (5), indicate a non-polar structure (compare Drew, J., 1929, 560; Lowry and Gilbert, *loc. cit.*),



so the parachor should indicate the presence of two singlet linkages by an anomaly of -24.8 units. All the substances, save (3), give an anomaly which is close to this value.

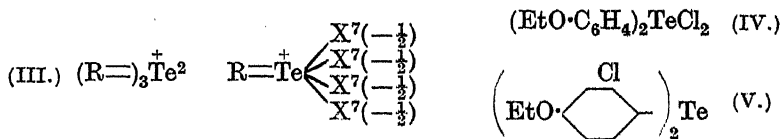
TABLE II.

*Quadrivalent Tellurium Compounds.*

Substance.	Formula.	[P] obs.	$\Sigma[P]$ .	Anomaly.
(1) Diphenyl telluridichloride	$(C_6H_5)_2TeCl_2$	547.3	568.0	-20.7
(2) Di- <i>p</i> -anisyl telluridichloride	$(MeO \cdot C_6H_4)_2TeCl_2$	663.2	686.0	-22.8
(3) $\alpha$ -Dimethyl telluridichloride	$Me_2TeCl_2$	282.5	300.2	-17.7
(4) $\alpha$ -Diethyl telluridi-iodide	$Et_2TeI_2$	425.0	451.6	-26.6
(5) $\beta$ -Diethyl telluridibromide	$Et_2TeBr_2$	377.3	405.6	-28.3

It has been shown by Drew (*loc. cit.*) that Vernon's  $\beta$ -compounds are probably dimerides with a polar structure, *i.e.*,  $(R_3Te)^+ (RTeX_4)^-$ . An electronic formula compatible with the octet rule may be written as in (III). Here both tellurium atoms have a complete octet and carry a positive charge; the anion contains four singlet-linked halogen atoms which give it a net charge of -1. On this view it will be seen that both the  $\alpha$ - and the  $\beta$ -compounds contain two singlet linkages per tellurium atom so that the parachors will give no distinction between the two series. The parachor found by Lowry and Gilbert for the last substance (see Table II) shows, as would be expected, much the same anomaly as the other quadrivalent tellurium compounds.

The substance described by Morgan and Drew (J., 1925, 127, 2307) as bis-*p*-phenetyl telluridichloride (IV) was also examined but proved to have very different properties from the corresponding anisyl compound (No. 2, Table II). The observed parachor, 731.2, is considerably lower than the value calculated for formula (IV), *viz.*, 739.2, but agrees well with the predicted value for formula (V), 729.8. The physical and chemical properties of this substance also



indicate that it is not a quadrivalent tellurium derivative but a nuclear-substituted diphenetyl telluride (V). Its melting point, 108°, is much lower than those of the diphenyl and dianisyl telluridichlorides, *viz.*, 160° and 182° respectively. Unlike the latter substance, the phenetyl compound is readily soluble in ligroin and cannot be reduced by zinc dust to the corresponding telluride. Furthermore, the phenyl and anisyl compounds are readily converted into telluroxides by aqueous alkali, but the phenetyl compound only gives up its chlorine slowly to boiling potash (Morgan and Drew, *loc. cit.*). We understand that further work on this and similar substances is now proceeding in Prof. Morgan's laboratory; meanwhile, from the evidence set out above we consider that formula

(V) gives the most probable structure of Morgan and Drew's phenetyl derivative.

### EXPERIMENTAL.

Surface tensions were determined by the method of maximum bubble pressure (Sugden, J., 1922, 121, 158; 1924, 125, 27) and densities by means of a U-shaped pyknometer (J., 1924, 125, 1171). The tables below are set out in our usual manner; the parachors are calculated by the formula  $P = M\gamma^{\frac{1}{2}}/D$ , where  $\gamma$  is the surface tension in dynes/cm., and  $D$  the density of the liquid, the density of the vapour being negligible.

*Diphenyl telluridichloride* ( $M = 352.5$ ). We are indebted to Prof. G. T. Morgan for a specimen of this substance. M. p. 160—161° (corr.). Densities determined:  $D_4^{62.8^\circ}$  1.618,  $D_4^{70^\circ}$  1.611,  $D_4^{77.5^\circ}$  1.603,  $D_4^{84.5^\circ}$  1.596, whence  $D_4^\circ = 1.785 - 0.00103t$ .

$t$ .....	167.5°	179°	189°	
$\gamma$ .....	39.47	38.23	37.17	
$D$ .....	1.613	1.601	1.591	
$[P]$ .....	547.6	547.4	547.0	Mean 547.3

*Di-p-anisyl telluridichloride* ( $M = 412.5$ ), prepared as described by Morgan and Kellett (J., 1926, 1085) and purified by several crystallisations from chloroform, was colourless and melted sharply at 182° (corr.). Densities determined:  $D_4^{186^\circ}$  1.544,  $D_4^{195.5^\circ}$  1.533,  $D_4^{206^\circ}$  1.523,  $D_4^{216^\circ}$  1.512, whence  $D_4^\circ = 1.734 - 0.00102t$ . The substance showed little sign of decomposition even at these high temperatures.

$t$ .....	186.5°	198.5°	211.5°	
$\gamma$ .....	37.82	36.49	35.57	
$D$ .....	1.543	1.530	1.517	
$[P]$ .....	663.0	662.5	664.0	Mean 663.2

*Di-p-anisyl telluride* ( $M = 341.6$ ) was obtained by Morgan and Kellett from the foregoing dichloride by reduction with zinc dust in benzene. A better yield (90%) was obtained by heating the dichloride in the water-bath with excess of zinc dust and glacial acetic acid; the filtered solution was poured into water and the precipitated telluride crystallised repeatedly from methyl alcohol; m. p. 53—54° (corr.). Densities determined:  $D_4^{92.5^\circ}$  1.515,  $D_4^{72^\circ}$  1.502,  $D_4^{52.5^\circ}$  1.492,  $D_4^{32.5^\circ}$  1.481, whence  $D_4^\circ = 1.582 - 0.00109t$ .

$t$ .....	76.5°	88.5°	100.5°	111°	121°	
$\gamma$ .....	40.60	38.84	38.75	36.68	35.63	
$D$ .....	1.499	1.486	1.473	1.461	1.450	
$[P]$ .....	575.1	574.0	576.1	575.4	575.5	Mean 575.2

*Dichlorodiphenetyl telluride* ( $M = 438.5$ ) was prepared as described by Morgan and Drew (*loc. cit.*) and crystallised from alcohol; m. p.

108° (corr.). Densities determined:  $D_4^{13.5^\circ}$  1.493,  $D_4^{14.5^\circ}$  1.482,  $D_4^{15^\circ}$  1.472,  $D_4^{16^\circ}$  1.462, whence  $D_4^\circ = 1.604 - 0.000979t$ .

$t$ .....	124.5°	136°	147.5°	157.5°	
$\gamma$ .....	37.52	35.93	35.12	34.12	
$D$ .....	1.482	1.471	1.459	1.450	
$[P]$ .....	732.1	729.9	731.7	731.0	Mean 731.2

*Phenoxtellurine* ( $M = 295.5$ ), prepared as described by Drew (J., 1926, 230), melted at 79° (corr.). Densities determined:  $D_4^{8.5^\circ}$  1.662,  $D_4^{10^\circ}$  1.645,  $D_4^{13.5^\circ}$  1.615,  $D_4^{14.5^\circ}$  1.602, whence  $D_4^\circ = 1.770 - 0.00117t$ .

$t$ .....	120.5°	132°	147°	
$\gamma$ .....	38.32	37.62	36.71	
$D$ .....	1.630	1.616	1.599	
$[P]$ .....	451.0	452.9	454.8	Mean 452.9

*Di-p-phenetyl ditelluride* ( $M = 497.1$ ), prepared by reduction of *p*-phenetyl telluritrichloride with aqueous bisulphite (Morgan and Drew, *loc. cit.*), crystallised from ligroin in orange-brown needles, m. p. 108° (corr.). As appreciable decomposition occurred when the substance was heated above its melting point, only one observation of the parachor was made. At  $t = 118^\circ$ ,  $\gamma = 34.44$ ,  $D = 1.666$ , whence  $[P] = 723.0$ .

*Di-n-butyl telluride* ( $M = 241.6$ ). This new substance was prepared as follows. The Grignard compound (2 mols.) from *n*-butyl bromide was added slowly to tellurium tetrachloride (1 mol.) suspended in dry ether. The mixture was heated for 2 hours on the water-bath, the ether distilled off, and the residue extracted with chloroform. The extract was shaken with water to decompose the excess of reagents and dried over calcium chloride, and the solvent removed. The residual red gum was dissolved in glacial acetic acid, and zinc dust added in slight excess. After a few minutes' heating on the water-bath, the solution was filtered and poured into water. The *telluride* then separated as a dark oil, which was dried over calcium chloride and distilled under diminished pressure in a stream of carbon dioxide. The product was a yellow oil, b. p. 132—135°/99 mm. (Found: Te, 52.5.  $C_8H_{18}Te$  requires Te, 52.8%); it possessed an unpleasant odour and oxidised on exposure to air. Exposure to light caused the yellow colour to deepen to a reddish tint.

Densities determined:  $D_4^{30^\circ}$  1.302,  $D_4^{35^\circ}$  1.294,  $D_4^{41^\circ}$  1.289,  $D_4^{46^\circ}$  1.284, whence  $D_4^\circ = 1.334 - 0.00109t$ .

$t$ .....	18°	28°	38°	
$\gamma$ .....	29.07	28.24	27.03	
$D$ .....	1.314	1.303	1.293	
$[P]$ .....	426.9	427.5	426.0	Mean 426.8

One of us (S. S.) is indebted to the Research Fund Committee of the Chemical Society which has partly defrayed the cost of this investigation.

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### XXXIV.—*The Photochemical Interaction of Acetaldehyde and Oxygen.*

By EDMUND JOHN BOWEN and EDMUND LAGESEN TIETZ.

IN 1835 Liebig (*Annalen*, **14**, 139) observed that acetaldehyde absorbed oxygen at the ordinary temperature, giving, according to him, acetic acid. Later, several investigators, working on "autoxidation," found that benzaldehyde and some other aldehydes gave peroxides with oxygen, but there seems to be no reference in the literature to the formation of a peroxide of acetaldehyde under these conditions. Chastaing (*Ann. Chim. Phys.*, 1877, **11**, 145) found that acetic acid was formed in the photochemical reaction.

The experiments now described show that a peroxide of acetaldehyde is quantitatively formed, and that it is a moderately stable substance; moreover, it is formed thermally as well as photochemically when liquid acetaldehyde is shaken with oxygen (*Nature*, 1929, **124**, 914). There are two possible peroxides, *viz.*, peracetic acid,  $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot\text{OH}$ , and diacetyl peroxide,  $\text{CH}_3\cdot\text{CO}\cdot\text{O}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$ , both of which have been prepared in other ways. The latter is hydrolysed to the former by water (Clover and Richmond, *Amer. Chem. J.*, 1903, **29**, 179). Bäckström (*Medd. K. Vetenskapsakad. Nobel-Inst.*, **6**, No. 16) has recently investigated the formation of a peroxide from benzaldehyde, and shown that the thermal and photochemical changes are chain reactions.

#### EXPERIMENTAL.

*Apparatus.*—A quartz mercury lamp contained in a water-cooled box served as a light source, and the light passed through a quartz window into a thermostat which contained the reaction vessel. This was made of clear fused quartz, joined to glass where necessary by mercury-sealed ground joints.

The purest specimens of acetaldehyde obtainable from Kahlbaum and Harrington were used, and the results were the same with either specimen.

1. *The Photochemical Oxidation of Gaseous Aldehyde by Air*.—A current of air, dried with sulphuric acid and filtered through glass wool, was drawn by a water-pump through a bubbler containing acetaldehyde at  $0^{\circ}$ , then through the quartz reaction bulb, and finally through potassium iodide solution. Iodine was liberated, showing that a peroxide had been formed by exposure of the gases to ultra-violet light. Control experiments showed that air alone passing through the reaction vessel did not liberate iodine, and that the excess aldehyde caught in the potassium iodide solution did not absorb any of the iodine liberated. The peroxide formed partly condensed in the reaction vessel, but by turning off the light and continuing the gas flow for several minutes the whole of it could be carried over. The temperature of the thermostat was  $20^{\circ}$  in the first experiments; it was later raised to  $30^{\circ}$  to diminish the time for "washing out" the peroxide after the light had been turned off. Experiments were made with rates of gas flow between 1000 and 20,000 c.c./hour, and it was found that at rates above 4000 c.c./hour the amount of peroxide formed was independent of the rate of flow, and linearly proportional to the time of exposure. The peroxide must be formed by a chain reaction, for the number of g.-mols. produced in these experiments per minute was about  $10^{-3}$ , whereas the energy in the light absorbed, calculated from an approximate knowledge of the energy distribution of the lamp and the absorption spectrum of acetaldehyde, was about  $10^{-6}$  g.-mol. quantum per minute. The chain length under these conditions was therefore about 1000 molecules, but the exact value of this is unimportant, as will be clear from section 2.

2. *Effect of Wave-length and Intensity of the Light*.—The above experiments were made with the full light of the mercury lamp. Experiments were next performed using screens to cut down the light intensity, in conjunction with filters. The screens were metal sheets with small perforations, and their transmissions were calibrated with a thermopile and an electric lamp. The following filters were used :

	Mercury lines transmitted.
(1) Vita-glass .....	>2900 Å.
(2) Auramine-O in aqueous solution (1 cm. of 0.0125%) .....	3135—2700
(3) Chlorine-bromine filter .....	2900—2485

The results are in Table I, where  $I$  represents the light intensity,  $y$  the titre against  $N/100$ -thiosulphate of the iodine liberated, and the filters used are denoted by their respective numbers in the foregoing scheme.

Table II gives the ratio of the mean titres to the square root of the light intensity, and shows clearly that the reaction is essentially

TABLE I.

Rate of flow of gases, 7000 c.c./hour. Time of exposure, 30 minutes.

I.	y.			I.	y.		
	(1).	(2).	(3).		(1).	(2).	(3).
48.5	29.08	54.29	32.14	16.0	16.19	30.72	18.57
	29.29	54.53	33.33		15.95	31.20	17.62
	28.06	54.05	30.71		15.71	30.48	17.62
23.3	18.33	36.91	21.67	7.5	10.24	21.91	13.33
	19.76	38.58	20.95		10.48	22.39	13.33
	19.05	37.62	20.83		10.48	20.95	12.86

TABLE II.

I.	$\sqrt{I.}$	$y/\sqrt{I.}$		
		(1).	(2).	(3).
48.5	6.96	4.14	7.80	4.61
23.3	4.83	3.95	7.81	4.38
16.0	4.00	3.99	7.70	4.49
7.5	2.74	3.74	7.94	4.80

the same throughout the ultra-violet absorption band of acetaldehyde, the rate being proportional to the square root of the light intensity. This is a rather surprising result.

3. *Effect of Acetaldehyde and of Oxygen Concentration.*—The aldehyde concentration was changed by introducing a variable by-pass and a flow-meter across the acetaldehyde bubbler, and the oxygen concentration was varied by using oxygen-nitrogen mixtures from cylinders, a large bottle being interposed to ensure mixing of the gases. The composition of the mixtures was obtained from flow-meter readings.

Table III gives the variation of the rate (as measured by the iodine titre,  $y$ ) with the relative aldehyde concentration,  $[A]$ , and Table IV the variation with oxygen concentration in the oxygen-nitrogen mixture.

TABLE III.

Exposure, 15 mins.

Vita-glass filter.				Chlorine-bromine filter.			
[A].	y.	[A].	y.	[A].	y.	[A].	y.
6.9	0.83	7.2	0.95	7.1	0.95	7.1	1.07
14.6	1.79	14.4	2.38	14.5	2.14	14.3	2.26
28.1	3.69	28.6	5.12	29.0	4.76	28.0	4.53
42.9	5.48	42.0	7.38	42.9	7.62	44.1	7.50
56.5	7.50	56.7	9.53	58.0	10.59	56.8	10.00
71.4	9.53	57.0	9.05	71.2	12.38	71.3	12.62
85.4	11.07	71.2	11.69	85.8	15.26	85.4	14.88
85.7	11.19	71.4	11.54	100.0	17.62	100.0	17.38
100.0	13.34	100.0	13.70				



TABLE IV.

Exposure, 30 mins. Full light.

O <sub>2</sub> , %.	y.	O <sub>2</sub> , %.	y.
24.1	40.2	53.3	35.0
34.2	39.0	62.3	35.7
41.5	39.0	74.0	36.4
47.8	34.8	100.0	38.3

From these results it appears that the reaction rate is proportional to the aldehyde concentration and independent of the oxygen concentration.

Before the mechanism of the reaction could be explained, it was necessary to know whether the variation of the rate with aldehyde concentration was due to variations in the amount of light absorbed. This was therefore examined at different wave-lengths by means of a quartz spectrograph of a new type, designed by Mr. J. H. Jeffree, in which a quartz sodium photoelectric cell and Lindemann electrometer are used to measure the light in the spectrum formed by the instrument, which had also been used to investigate the transmissions of the filters described above. Between 3200 and 2800 Å., the absorption of gaseous acetaldehyde in the photochemical cell was about 90%, and between 2700 and 2400 Å. about 74%. The absorption was almost independent of the aldehyde concentration, showing that most of the mercury lines in the above regions were totally absorbed, the others being transmitted.

The kinetics of the reaction are  $dx/dt = k\sqrt{L}[A]$ , where  $L$  is the light absorbed, and  $[A]$  the aldehyde concentration. An explanation of this result can be given by the following chain mechanism :

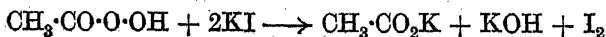
	Rate.
1. $A + h\nu \longrightarrow A^*$	$k_1 L$
2. $A^* + O_2 \longrightarrow AO_2^*$	$k_2 [A^*][O_2]$
3. $AO_2^* + A \longrightarrow A^* + AO_2$	$k_3 [AO_2^*][A]$
4. $2AO_2^* \longrightarrow ?$	$k_4 [AO_2^*]^2$

Reactions 2 and 3, by repetition, produce chains, which are broken by reaction 4. For the steady reaction, we have

$$\begin{aligned} d[A^*]/dt = 0 &= k_1 L + k_3 [AO_2^*][A] - k_2 [A^*][O_2] \\ \text{and } d[AO_2^*]/dt = 0 &= k_2 [A^*][O_2] - k_3 [AO_2^*][A] - k_4 [AO_2^*]^2 \\ \text{whence } k_1 L &= k_4 [AO_2^*]^2 \end{aligned}$$

$$\text{Then } d[AO_2]/dt = k_3 [AO_2^*][A] = k_3 \sqrt{L} \sqrt{k_1/k_4} [A]$$

When peracetic acid reacts with potassium iodide the solution should become alkaline :



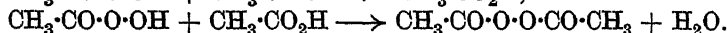
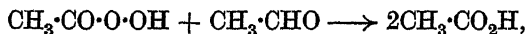
Experiments showed, however, that after the iodine titration the

solution was always slightly acid. This point is referred to again in section 4.

4. *Oxidation in the Liquid and the Dissolved State.*—The apparatus used for these experiments consisted of a small quartz tube to contain the liquid, mounted in a shaking machine in a thermostat, and connected by flexible tubing to a gas burette containing oxygen. As solvents, water, acetic acid, and hexane were tried, as they are transparent to the light absorbed by acetaldehyde. The peroxide was estimated by adding the liquid to potassium iodide solution as before, and was found to be formed very rapidly in liquid aldehyde and in its solutions in the above three solvents, and once formed, to be very stable, showing no decomposition in one hour, except in the aqueous solutions, in which it almost all reacted in 20 seconds. This latter fact was utilised to determine the nature of the peroxide. Liquid aldehyde was shaken with oxygen to produce some peroxide. One portion (a) was added at once to neutral potassium iodide solution, the liberated iodine titrated with *N*/100-thiosulphate, and the remaining acidity estimated with *N*/100-baryta solution. The other portion (b) was added to water, and the peroxide allowed to react with the excess aldehyde to give acetic acid. The acidity of this solution was then estimated. The following table gives some results:

Portion.	Expt. 1.		Expt. 2.	
	Iodine titre.	Acid titre.	Iodine titre.	Acid titre.
(a) .....	24.97	8.28	25.32	7.56
(b) .....	0.0	45.77	0.0	46.68

These figures can be explained by assuming that the peracetic acid first formed partly reacts with aldehyde to give acetic acid, but that the reaction is limited by the combination of the acetic acid with peracetic acid to give diacetyl peroxide, according to the equations



Diacetyl peroxide reacts with potassium iodide to give a neutral solution:  $(\text{CH}_3\cdot\text{CO}\cdot\text{O})_2 + 2\text{KI} \longrightarrow 2\text{CH}_3\cdot\text{CO}_2\text{K} + \text{I}_2$ , and the average iodine titre value above (25.15 c.c.) represents 12.57 c.c. of *N*/100-peroxide. The average acid titre after the iodine titration (7.92 c.c.) probably represents a little excess acetic acid. The increase in acidity on standing in aqueous solution should then be represented by  $46.22 - 7.92 = 38.3$  c.c. of *N*/100-acid. The reaction of the peroxide on standing in water must be  $(\text{CH}_3\cdot\text{CO}\cdot\text{O})_2 + \text{CH}_3\cdot\text{CHO} \longrightarrow 3\text{CH}_3\cdot\text{CO}_2\text{H}$ , representing an acidity of  $3 \times 12.57 = 37.71$  c.c. of *N*/100-acid, in close agreement with the calculated figure, 38.3 c.c.

It seems necessary to assume the formation of diacetyl peroxide to account for the approximate neutrality of the solutions after titration of the iodine liberated. The results given in Table VI for hexane-aldehyde mixtures show an even greater approach to neutrality than the figures just given.

Although the peroxide was found to be quite stable when formed in pure liquid aldehyde, the reaction rates were very irregular, due to the high vapour pressure, which, by producing a buffer of vapour, prevented the oxygen from freely dissolving in the liquid. The absorption of oxygen also took place rapidly in the dark. Very reproducible results were obtained for solutions of acetaldehyde in glacial acetic acid and in hexane. The thermal reaction in these solvents was small. Table V gives some results for acetic acid solutions, the amounts of oxygen absorbed (as given by gas-burette readings), and of peroxide formed ( $\text{AO}_2$ , as deduced from the iodine titre) being recorded as g.-mols.  $\times 10^{-4}$ .

TABLE V.

Ratio, by vol., $\text{C}_2\text{H}_4\text{O} : \text{C}_2\text{H}_4\text{O}_2$ .	Time, mins.	$\text{O}_2 \times 10^4$ .	$\text{AO}_2 \times 10^4$ .
1 : 1	1	1.72	1.45
	2	3.08	2.51
	3	4.27	3.36
	4	4.87	3.89
(Dark reaction	15	0.35	0.28)
1 : 2	1	1.64	1.51
	3	4.85	4.43
	5	7.56	6.30
(Dark reaction	15	0.39	0.39)
1 : 5	1	1.20	1.44
	2	2.34	2.54
	3	3.03	3.07
	5	4.72	4.45
	7	7.38	6.50
(Dark reaction	15	0.05	0.27)
1 : 8	2.5	1.47	1.61
	5	3.34	3.22
	7	4.44	4.10
	10	6.24	5.50
	15	6.77	6.01
(Dark reaction nil.)			
1 : 10	2.5	0.89	0.99
	5	2.15	2.13
	7	2.72	2.56
	10	3.78	3.50
	15	6.30	5.33
(Dark reaction nil.)			

These results show that the amount of peroxide formed increases linearly with time, and that the rate is proportional to the aldehyde concentration when it is below 20%. The most important result, however, is the agreement between the number of molecules of oxygen absorbed and of peroxide produced. In acetic acid solutions,

diacetyl peroxide formation can occur without the preliminary decomposition of some of the per-acid by reaction with aldehyde.

Table VI gives results for hexane solutions. The light intensity was varied with screens as previously described, and its relative values are denoted by  $I$ . The iodine titre  $y$  (c.c. $N$ /100-thiosulphate) is a measure of the peroxide produced.

TABLE VI.

Ratio, by vol., $C_2H_4O : C_6H_{14}$ .	$I$ .	$y$ .	$y/\sqrt{I}$ .	Excess acidity after iodine titre (c.c. $N$ /100).
1 : 2	48.5	69.1	9.93	4.5
	23.3	45.0	9.32	2.5
	16.0	41.6	10.4	2.0
	7.5	26.8	9.77	2.0
1 : 3	48.5	42.3	6.08	2.5
	23.3	28.7	5.94	2.0
	16.0	27.3	6.82	2.0
	7.5	21.4	7.81	2.0
1 : 5	48.5	25.6	3.68	0.3
	23.3	18.4	3.81	0.0
	16.0	14.6	3.65	0.0
	7.5	10.8	3.94	0.0

These results are in complete agreement with those of Tables I and II, and show that the rate of peroxide formation is proportional to the square root of the light intensity and to the aldehyde concentration. The amount of free acid found after the iodine titre is small, showing that diacetyl peroxide is probably formed.

5. *The Inhibition by Ethyl Alcohol*.—The introduction of an inhibitor into the system will alter the chain-breaking mechanism from the bimolecular reaction  $2AO_2^* \longrightarrow ?$  to one of the type  $AO_2^* + X \longrightarrow ?$ . The rate of reaction will then become proportional to the light intensity instead of to its square root. That this is actually the case is shown in Table VII, which gives results for the rate when alcohol was added.

TABLE VII.

Ratio by volume. Aldehyde:hexane:alcohol = 2 : 4 : 1.						
$I$ .....	4.85	4.85	2.33	2.33	1.60	1.60
$y$ .....	33.9	34.1	16.4	16.6	11.5	11.3
$y/\sqrt{I}$ .....	6.99	7.03	7.04	7.19	7.19	7.07

From this result it is apparent that the effectiveness of an inhibitor at a given concentration must depend on the light intensity in this reaction. Assuming that the mechanism of inhibition is that described above, it can be shown that for fixed light intensity and aldehyde concentration the rate should vary according to the equation  $y^2 + \alpha Xy = \beta$ , where  $y$  is the rate and  $X$  the inhibitor con-

centration; whereas for fixed light intensity and inhibitor concentration, the ratio of rate to aldehyde concentration should be constant. These conclusions are tested by the results given in Tables VIII and IX, for solutions in hexane. The former table gives  $X$  as the percentage of alcohol,  $y$  as the iodine titre, and the value of  $\alpha$  as calculated from the above equation with  $\beta = 5242$ .

TABLE VIII.

Aldehyde concentration, 33%.

$X$ .	$y$ .	$\alpha$ .
0	72.4	—
1.33	55.5	29.3
6.67	29.1	22.6
12.5	11.3	36.3

TABLE IX.

Alcohol concentration, 14.3%.

$[A]$ .	$y$ .	$[A] - 14.3$ .
14.3	1.9	0
21.42	6.1	7.1
28.56	10.5	14.3
35.7	22.0	21.4

Although the variation of velocity with inhibitor concentration is approximately as expected, yet its variation with aldehyde concentration can only be made to agree with the theory if the inhibitor concentration is subtracted from the aldehyde concentrations (see Table IX). The interpretation of this is that the alcohol first combines with activated aldehyde molecules to give a compound which is the actual inhibitor, thereby reducing the effective aldehyde concentration. These experiments are being continued.

6. *Static Measurements on Gaseous Mixtures.*—It was suggested to us by Mr. A. C. Egerton that, as peroxides are formed as intermediate compounds in the oxidation of hydrocarbons, experiments on the effect of "anti-knock" substances on this reaction would be interesting. For this purpose, gaseous mixtures of acetaldehyde and oxygen at total pressures between 60 and 20 cm. of mercury were introduced into a quartz bulb connected to a mercury manometer, and the reaction was followed by the diminution of pressure which occurs when the mixture is exposed to ultra-violet light. The pressure change-time curves for the complete reaction were found to begin with a long linear portion. When the ratio of acetaldehyde to oxygen was greater than 3:2, the rate after the initial period fell off gradually to an end-point, while when the ratio was less than this, the end-point was approached abruptly. Tables of results for these measurements are not given because a complete explanation depends on the nature of the final products, which were found by analysis to be complex, and to contain carbon dioxide, monoxide, and acetic acid. The initial rate of reaction was found to be approximately proportional to the square root of the light intensity and to the aldehyde pressure, and independent of the oxygen pressure, in agreement with the results derived from estimation of the peroxide.

The effect of introducing small quantities (0.1—5 mm.) of the vapour of anti-knock substances was as follows.

*Iron carbonyl.* A dense white mist was formed when the light was turned on. The oxidation of the aldehyde was inhibited for a long period, proportional to the amount of iron carbonyl present. At the end of the induction period the mist practically disappeared, and the reaction suddenly began at a rate almost equal to its value in the absence of the inhibitor. A red powder ( $\text{Fe}_2\text{O}_3$ ?) was left in the reaction vessel.

*Nickel carbonyl.* The quantity introduced, owing to the higher vapour pressure, was about ten times that of iron carbonyl. A dense mist was formed, and a white solid deposited, and the reaction was inhibited completely.

*Selenium diethyl.* A dense mist was again formed, but no induction period was produced; instead, the reaction proceeded at a slow rate which gradually increased as the mist disappeared. Great difficulty was experienced in removing the last traces of selenium compounds from the reaction vessel after these experiments.

*Lead tetraethyl.* The vapour of this substance had no effect on the reaction rate.

*Ethyl iodide.* The introduction of this substance decreased the rate of reaction greatly, without producing any induction period.

These results show that anti-knock substances do not all act as inhibitors for this reaction. Lead tetraethyl does not affect the reaction at all. The results for ethyl iodide can be explained as an inner filter effect. It is uncertain whether iron and nickel carbonyls act as direct inhibitors or whether the mist formed merely scatters the light. The most that can be said is that an apparently equally heavy mist is formed with selenium diethyl, without the production of an induction period. The inhibiting effect of iron carbonyl is inversely proportional to the aldehyde pressure, which is some evidence that it acts as a direct chain breaker.

#### *Summary.*

1. A peroxide is formed when gaseous, liquid, or dissolved acetaldehyde is exposed in presence of oxygen to ultra-violet light. The reaction has been examined in different spectral regions. In the liquid and the dissolved state the peroxide is also formed in the dark.

2. The rate of reaction is proportional to the square root of the light intensity and to the aldehyde concentration, but independent of the oxygen concentration. This can be explained by a chain mechanism involving the formation of peracetic acid as the first product.

3. Reasons are given to show that diacetyl peroxide is formed by further reactions of the peracetic acid.

4. Alcohol acts as an inhibitor when added to hexane solutions of aldehyde. As expected, the rate becomes directly proportional to the light intensity, instead of to its square root.

5. Anti-knock substances do not all act as inhibitors of the photochemical reaction between acetaldehyde and oxygen.

We are indebted to Mr. Egerton for the anti-knock substances, and to the Royal Society for a grant to purchase the quartz spectrograph used in this work.

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### XXXV.—*Extinction of Methane Flames by Water Vapour.*

By HUBERT FRANK COWARD and JOHN JEBSON GLEADALL.

THE limits of inflammability of methane in air are narrowed by the progressive addition of an inert gas to the air. Data for the effect of carbon dioxide, nitrogen, argon, and helium have been published (Coward and Hartwell, J., 1926, 1522). To these is now added a series of results obtained with water vapour, for which no data of any moment have hitherto been recorded.

#### EXPERIMENTAL.

For observations on the limits of inflammability of gas mixtures, it is desirable to use a vessel which is both wide enough to avoid errors due to cooling by its walls and long enough to show whether flame travels independently of the initial impetus of the source of ignition. Constant pressure should be maintained during inflammation, if the observations are to have any precise significance. Experience has shown ("Limits of Inflammability of Gases and Vapors," by H. F. Coward and G. W. Jones, *U.S.A. Bureau of Mines*, Bull. 279, 1928) that a vertical tube 2 inches in diameter, 4—6 feet long, and opened at the end behind the flame at about the moment of ignition, meets these requirements; it gives results nearly the same as those obtained in very much larger apparatus. The source of ignition is preferably near the lower end of the tube, for certain weak mixtures, although capable of indefinite propagation of flame upwards, are unable to burn downwards.

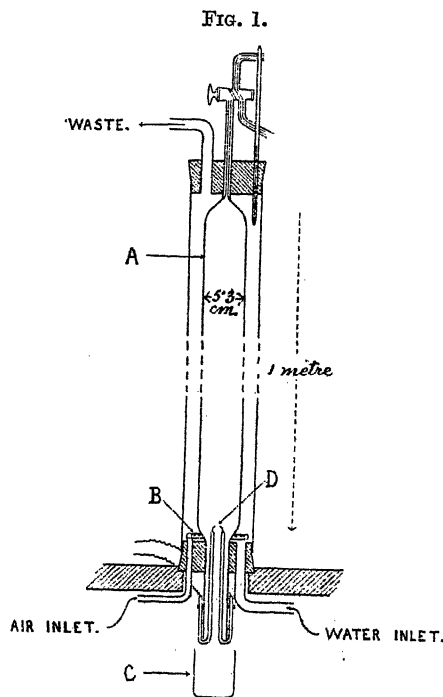
These requirements are met readily when gases alone are under examination, but not so easily when the temperature of the con-

tainer has to be above the normal to avoid condensation of vapours. Fig. 1 shows the arrangement which has proved satisfactory with mixtures of methane, air, and water vapour up to the temperature (just above  $67^{\circ}$ ) necessary to maintain enough water vapour to extinguish flame in any mixture of methane and air.

The glass tube A was surrounded by a stream of hot water from a gas heater. The water jacket was covered, save for a vertical observation slit, with asbestos cloth, and the water was stirred by

air bubbles from the perforated tube B. The difference in temperature between the top and bottom of the water jacket was never more than  $0.2^{\circ}$ .

For an experiment, the tube A was filled with water and water-sealed by the beaker C. The jacket and the beaker were brought to a predetermined temperature which was then maintained constant. The air bubble which had appeared at the top of A was sucked off, and the prepared mixture of methane and air admitted through the tap and finally bubbled through the water in C until about twice the volume of A had passed. A piece of tape, held by thin stainless-steel springs against the inner



wall of A, maintained liquid water in contact with the gas throughout the length of the tube.

The inflammability of the mixed methane, air, and water vapour was tested, when it had been heated by the constant-temperature jacket for 10 minutes, by passing a "fat" spark from an induction coil across the 5 mm. gap at D.\* At the same moment the beaker C was withdrawn to permit ready escape of the expanded products of combustion. An inflammable mixture propagated a blue flame with

\* Such a spark is strong enough to ensure ignition of any methane-air mixture which is capable of propagating flame—its energy much exceeds the minimum for ignition.



a convex front throughout the whole tube above the spark gap; if the mixture were outside the limits of inflammability, a cap of flame appeared above the spark gap, but did not assume the characteristic shape of the flame in a mixture which is inflammable *per se*, nor did it extend far up the tube. The distinction was clear.

In calculating the composition of the mixture, the ratio of methane to air was obtained by analysis of a sample from the gas holder. The total pressure of the mixture was atmospheric, and the partial pressure of the water vapour was assumed equal to the saturation pressure of water at the temperature of the jacket. The only place where the temperature of the tube A might have been somewhat lower was in and just below the rubber stopper, but, as the mixture at that place would be heavier than the rest, its influence on the composition of the mixture near and above the spark would be inappreciable.

It was possible that radiation from the advancing flame might evaporate some moisture from the tape and from the walls of the tube, just ahead of the flame, and thus produce a mixture of greater water content than we had calculated. To test this point, the tape was removed and a lower-limit mixture was passed through until only a few large drops of water, and (in one experiment) one patch of smaller drops, remained. The mixture was kept until it was saturated, and then ignited; the flame which travelled up the tube showed no change in width or shape as it passed the wet places. In other tests a small length of tape was inserted in the tube. The tape remained wet during the test, but the flame was not affected as it approached or passed the tape. It is concluded that evaporation of water by the flame was without appreciable influence on the limits.

*Results.*—The limits of inflammability of methane in dry air, in the 3-foot tube of the apparatus described, the water in the vessel C being replaced by mercury, were 5.24 and 14.08%. These agree sufficiently well with the previous observations in a 6-foot tube, *viz.*, 5.24 and 14.02%.

The results which serve to define the limits of mixtures of water vapour, methane, and air are in Table I. As the method of experiment is by trial and error, the range between inflammable and non-inflammable mixtures being narrowed in successive experiments, only the last few results of each series are quoted. When the figures of the first four columns of the tables are plotted on a large-scale diagram, the choice of the figures for the limit mixtures, shown in cols. 5 and 6, becomes clear. The concentration of water vapour is expressed as a percentage on the "original atmosphere" of air water vapour; whereas that of methane is expressed as

a percentage of the whole, *i.e.*, methane *plus* air *plus* water vapour.

TABLE I.

Propagated flame.		Failed to propagate flame.		Limit mixture.		Temp. (approx.).
Water vapour.	CH <sub>4</sub> .	Water vapour.	CH <sub>4</sub> .	Water vapour.	CH <sub>4</sub> .	
21.4	5.97	21.2	5.91*	21.2	5.90	60°
21.3	5.94	21.3	5.90*			
21.2	5.89*	21.3	5.88*			
21.2	5.89*	21.2	5.84			
		21.3	5.81			
26.4	6.43	26.5	6.33	26.4	6.34	64—65
26.4	6.34	26.6	6.32			
29.0	6.87	29.1	6.86	29.1	6.86	67
29.0	6.86	29.1	6.84			
28.9	7.19	29.2	7.17	29.0	7.18	67
23.9	8.42	24.0	8.40	23.9	8.41	62
23.9	8.41	24.1	8.39			
		24.1	8.39			
19.6	9.28	19.6	9.36	19.5	9.37	57.5
19.5	9.34	19.5	9.40			
19.4	9.36	19.6	9.42			

\* These five mixtures are scarcely distinguishable one from another, analytically. We estimate the accuracy of the water figure as within 0.2 unit and of the methane figure as within 0.02 unit.

Fig. 2 contains a graph of the limits given in Table I, with lower and higher limits for mixtures saturated with water vapour at laboratory temperature (see Coward and Hartwell, *loc. cit.*, footnote p. 1523). The curves for carbon tetrachloride (Coward and Jones, *Ind. Eng. Chem.*, 1926, 18, 970) and other diluent gases are included. The broken line is the locus of mixtures in which the molecular ratio CH<sub>4</sub> : O<sub>2</sub> is 1 : 2.

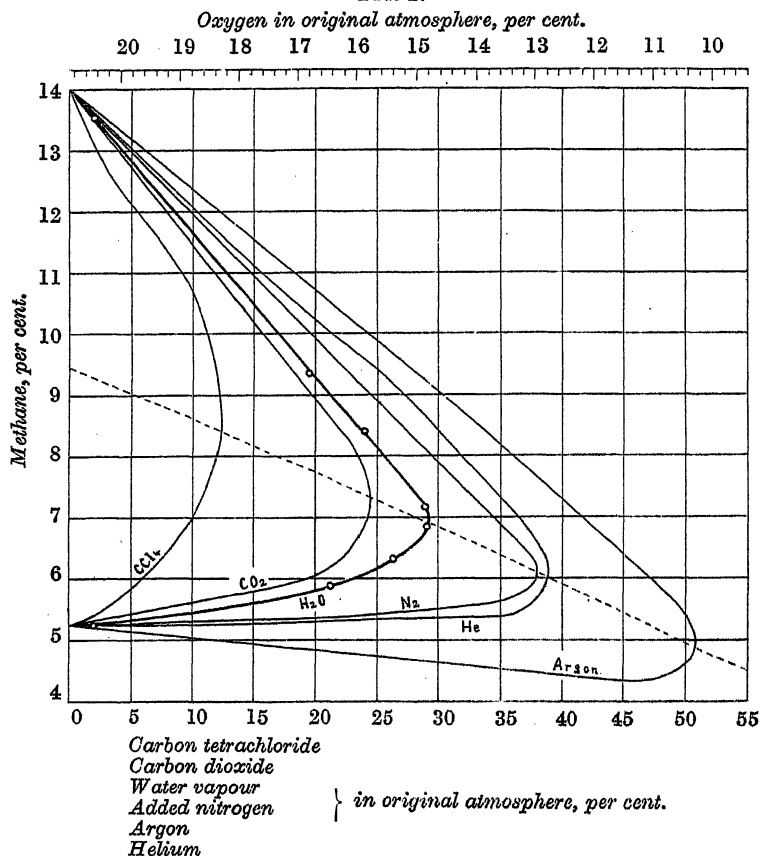
Most of the points on the water-vapour curve were necessarily obtained at temperatures higher than that of the laboratory. The points nearest the "nose" of this curve, for example, were obtained at 67°. For comparison, therefore, the position of the "nose" of the carbon dioxide curve was determined at the same temperature, and found to lie at 27.1% of carbon dioxide, instead of 24.5% at 17°. The "nose" of the nitrogen curve would doubtless be extended similarly by the same increase of temperature. Water vapour therefore lies between carbon dioxide and nitrogen in its extinctive action on methane flames, and is very nearly as effective, volume for volume, as the former.

#### Discussion.

The extinctive action of five of the six diluent gases runs in the order of their molecular heat capacities, which are (*C<sub>p</sub>*, 0—1200°):

Carbon tetrachloride, 22 (estimated); carbon dioxide, 10.90; water vapour, 9.20; nitrogen, 7.21; argon, 5.0. Helium is exceptional, for its heat capacity is equal to that of argon, but its extinctive effect on flame is relatively much greater. This is ascribed to its abnormally high thermal conductivity.

FIG. 2.



The extinctive action of water vapour is rather greater than would be inferred from its specific heat. The actual heat capacity of the water vapour present in the limit mixtures is, however, relatively greater than the figure 9.20 would suggest; for, according to Bose (*Z. Elektrochem.*, 1908, 14, 269), saturated water vapour is about 8.5% associated at 67°. Allowance being made for this and for the heat of dissociation of the complex water molecules ( $\text{H}_4\text{O}_2 = 2\text{H}_2\text{O} - 9640$  cal.; Bose, *loc. cit.*), the relative heat capacity of water vapour would be nearly 10.0 in the series.

The incidence of the water-gas equilibrium, which is attained in the gases "snatched" from the centre of higher-limit flames of methane, oxygen, and nitrogen (Coward, *Fuel*, 1929, 8, 470), has but a small effect on the heat of reaction, the heat capacity, and the thermal conductivity of the mixture. The effects of alterations in these three factors, due to the water-gas reaction, may be shown nearly to cancel one another.

The conclusion is, therefore, that, in the relative extinctive effects on methane flames of diluent gases which take no important part in the flame reactions, the chief factor is the heat capacity of the diluent, but that helium stands in an exceptional position by virtue of its high thermal conductivity. Other factors have very little influence. Carbon tetrachloride, although it undergoes extensive reaction in the flame of a methane-air mixture, falls into line with the other diluent gases.

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SHEFFIELD.

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### XXXVI.—*Mobile Anion Tautomerism. Part IV. The Stability of Some $\alpha$ - and $\gamma$ -Alkylallyl Alcohols and their Esters. 2:4-Dimethylcinnamyl Alcohol.*

By HAROLD BURTON.

It has been emphasised in previous parts of this series that the migratory power of X in the simple three-carbon anionotropic system, (I)  $R\cdot CHX\cdot CH:CH_2 \rightleftharpoons R\cdot CH:CH\cdot CH_2X$  (II), depends on three factors: (i) the group R, (ii) some molecular property of the solvent closely related to the dielectric constant, and (iii) the anionic stability of X (i.e., strengths of the acids HX). With regard to factor (iii), the migratory power of X is in the order  $Br > O\cdot CO\cdot CCl_3 > O\cdot CO\cdot C_6H_4\cdot NO_2(p)$ ;  $OAc > OH$ , the position of the trichloroacetoxy-group following from the recent work of Prévost (*Ann. Chim.*, 1928, 10, 160). Prévost has shown that esterification of trichloroacetic acid with either methylvinylcarbinol,  $CHMe(OH)\cdot CH:CH_2$ , or crotyl alcohol,  $CHMe\cdot CH\cdot CH_2\cdot OH$ , gives in each case the same mixture of about 55% of methylvinylcarbinyl trichloroacetate and about 45% of crotyl trichloroacetate. Furthermore, the action of potassium trichloroacetate on crotyl bromide

( $\alpha$ -bromo- $\Delta^{\beta}$ -butene) also gives the same mixture of the isomeric trichloroacetates. The explanation advanced by Prévost to account for the formation of the same mixture is that "trichloroacetic acid esterifies solely by the effect of hydrogen ions in liberating the tri-polar ion  $\text{CH}_3\cdot\overset{+}{\text{CH}}\cdot\bar{\text{C}}\text{H}\cdot\overset{+}{\text{CH}}_2$ ; the trichloroacetoxy-group subsequently combining at one or other of the positive poles."

An alternative explanation is that the esters of types I and II are first formed and that these subsequently undergo interconversion to give an equilibrium mixture. It is probable that Prévost considered this aspect, since he states that the isomeric trichloroacetates are not isomerised even above  $100^\circ$ . No experimental details of the attempted interconversions are given and one may presume that Prévost merely heated the esters alone below their boiling points. Consideration of the experimental conditions under which esterification is carried out indicates that the mixture of either alcohol and trichloroacetic acid would have a moderately high dielectric constant; this would tend to decrease as reaction proceeded. In Prévost's experimental procedure, esterification is far from complete (yield of esters, 45–46%), so that rearrangement of the isomeric trichloroacetates would be expected to occur if such an explanation is the correct one. On the other hand, the dielectric constants of the pure esters would be relatively small and long heating would be necessary to effect any interconversion (see Burton, J., 1928, 1650).

The author's method (*loc. cit.*) being used, methylvinylcarbinyl and crotyl trichloroacetates were heated in acetic anhydride (dielectric constant = 20.5) for 6 hours at the boiling point; in each case the equilibrium mixture of about 55% of the former and 45% of the latter ester was obtained. This shows definitely that the explanation suggested above is probably the correct one, and that Prévost's failure to effect isomerisation was due to unsuitable experimental conditions.

It would be expected that esterification of trichloroacetic acid with butylvinylcarbinol would afford a mixture with the equilibrium displaced in the direction II. Unfortunately, this has not been capable of verification, as the attempted esterification gave rise to none of the expected esters.

In Part III (J., 1929, 455) it was pointed out that the influence of the  $n$ -alkyl group in activating the simple three-carbon anionotropic system should reach its maximum at about  $n$ -hexyl. It was also stated that "even then the activation may not be as great as that produced by the phenyl or by *gem*-dialkyl groups." It is now shown that the  $n$ -hexyl and *iso*amyl groups are very similar to the

methyl group in their activating power. For instance,  $\alpha$ -n-hexylallyl *p*-nitrobenzoate, like  $\alpha$ -methylallyl *p*-nitrobenzoate, is recovered unchanged when an acetic anhydride solution is boiled for 6 and 24 hours; and acetylation of  $\alpha$ -isoamylallyl alcohol with an excess of acetic anhydride gives the corresponding acetate, as does methylvinylcarbinol. The pronounced difference in activating power of the alkyl and the phenyl group is again emphasised in experiments with  $\alpha$ -m-4-xylylallyl alcohol, which are described in the experimental portion. The conversion of this alcohol into 2:4-dimethylcinnamyl alcohol is of interest in view of the very limited methods available for the synthesis of cinnamyl alcohols.

#### EXPERIMENTAL.

Methylvinylcarbinol and butylvinylcarbinol were prepared by Delaby's method (*Compt. rend.*, 1922, 175, 967).

Butylvinylcarbinyll *p*-nitrobenzoate, prepared by the pyridine method, crystallises from cold alcohol in colourless plates, m. p. 24—25° (Found: C, 63.8; H, 6.5.  $C_{14}H_{17}O_4N$  requires C, 63.9; H, 6.5%).

*Esterification of Trichloroacetic Acid with Methylvinylcarbinol.*—This was carried out in the manner described by Prévost (*loc. cit.*). The yield of mixed esters, b. p. 70—90°/10 mm., was 45—46%. Fractionation of the mixture in a vacuum, by means of a Dufton column (50 cm.), gave approximately equal amounts of two well-defined fractions, the mid-piece being rejected. Further distillation under reduced pressure and collection of the middle fractions only, afforded methylvinylcarbinyll trichloroacetate, b. p. 69.5—70.5°/8 mm.,  $n_{D_{461}}^{18}$  1.46390 (Found: C, 33.4; H, 3.0. Calc.: C, 33.1; H, 3.2%), and crotyl trichloroacetate, b. p. 86—86.5°/9 mm.,  $n_{D_{461}}^{18}$  1.47596 (Found: C, 33.4; H, 3.4%). The refractive indices were measured with a Pulfrich instrument, the green line of the mercury arc being used, with an auxiliary slit to increase the accuracy of setting. The drum of the instrument was used, so the differences between the observed indices are more accurate than the absolute values. The pure esters and mixtures were measured rapidly one after another at the same temperature. The mixtures obtained from three similar experiments showed  $n_{D_{461}}^{18}$  1.46947, 1.46947, and 1.46932 respectively; hence content of methylvinylcarbinyll trichloroacetate = 54, 54 and 55% respectively.

*Conversion of the Esters into the Equilibrium Mixture.*—Either of the esters (10 g.) was boiled with acetic anhydride (20 c.c.) for 6 hours. The yellow solution was poured into water and extracted with ether, and the extract was washed repeatedly with sodium

\* The values for C are all somewhat high owing to the large chlorine content of the esters.

carbonate solution until free from acid and dried. The residue from the ethereal extract gave, in addition to a main fraction, b. p. 70—90°/10 mm., high-boiling material, showing that some decomposition had taken place. The mixed esters were redistilled three times and analysed (Found: C, 33.6, 33.5; H, 3.1, 3.5%). The refractive indices of the mixtures were 1.46916 and 1.46932; hence content of methylvinylcarbinyl trichloroacetate = 56 and 55%.

*α-n-Hexylallyl Alcohol* ( $\Delta^a$ -Nonen- $\gamma$ -ol),  $C_6H_{13}\cdot CH(OH)\cdot CH\cdot CH_2$ .—The Grignard reagent prepared by the method of Gilman and McCracken (*J. Amer. Chem. Soc.*, 1923, 45, 2463) from magnesium (12 g.), *n*-hexyl bromide (82 g.), ether (200 c.c.), and a trace of iodine was cooled below 0°, and a solution of acraldehyde (33 c.c.) in ether (150 c.c.) added during 2 hours. The mixture was stirred for a further 4 hours and then decomposed with ice and saturated ammonium chloride solution. Distillation of the oil from the ethereal extract gave 36 g. of a mobile oil, b. p. 88—95°/16 mm., which gave high values for carbon and hydrogen and was not purified by further fractionation. When the oil was heated with *p*-nitrobenzoyl chloride (50 g.) and pyridine (350 c.c.) on the water-bath for 2 hours, and the mixture poured on ice, a solid (35 g.) was obtained. This was collected, washed with cold light petroleum, drained on porous earthenware, and crystallised from a concentrated alcoholic solution at 0—5°; *α-n-hexylallyl p-nitrobenzoate*, m. p. 36—37°, then separated in almost colourless plates (Found: C, 65.8; H, 7.2.  $C_{16}H_{21}O_4N$  requires C, 66.0; H, 7.2%).

Hydrolysis of the *p*-nitrobenzoate (14.5 g.) by boiling with 5% alcoholic potassium hydroxide solution (100 g.) for 2 hours, the product being worked up in the usual way, gave *α-n-hexylallyl alcohol* as a colourless mobile oil, b. p. 89°/12 mm. (Found: C, 75.7; H, 12.8.  $C_6H_{13}O$  requires C, 76.05; H, 12.7%).

When the *p*-nitrobenzoate (5 g.) was boiled with acetic anhydride (10 c.c.) for 6 and for 24 hours, and the solutions were poured into water, unchanged material was obtained in each case.

*α-isoAmylallyl Alcohol*,  $CHMe_2\cdot CH_2\cdot CH_2\cdot CH(OH)\cdot CH\cdot CH_2$ .—The Grignard reagent prepared from magnesium (12 g.), *isoamyl* bromide (76 g.), ether (300 c.c.), and a trace of iodine was treated during 2 hours with a solution of acraldehyde (30 c.c.) in ether (150 c.c.) as for the hexyl analogue. Decomposition of the product with ice and ammonium chloride and careful fractionation of the product obtained afforded 14 g. of the *alcohol*, b. p. 73—74°/16 mm., as a colourless mobile oil (Found: C, 75.05; H, 12.6.  $C_8H_{16}O$  requires C, 75.0; H, 12.5%). A crystalline *p*-nitrobenzoate could not be prepared by the pyridine method.

*α-isoAmylallyl acetate*,  $CHMe_2\cdot CH_2\cdot CH_2\cdot CH(OAc)\cdot CH\cdot CH_2$ , was

obtained by boiling a mixture of the above alcohol (14 g.) and acetic anhydride (20 c.c.) for 9 hours and working up the product in the usual way. The ester is a colourless mobile oil, b. p. 83—84°/18 mm. (Found: C, 70·5; H, 10·6.  $C_{10}H_{18}O_2$  requires C, 70·6; H, 10·6%). Hydrolysis with an excess of boiling 5% alcoholic potassium hydroxide solution regenerated the above alcohol.

*α-m-4-Xylylallyl Alcohol*,  $C_6H_3Me_2\cdot CH(OH)\cdot CH:CH_2$ .—To the well-cooled Grignard reagent prepared from magnesium (12 g.), *m-4*-iodoxylylene (116 g.), ether (200 c.c.), and a trace of iodine, a solution of acetaldehyde (33 c.c.) in ether (150 c.c.) was added during 2 hours. The mixture was stirred for a further 3 hours, and the very gummy product decomposed with ice and ammonium chloride solution. Distillation of the residue from the ethereal extract afforded a fraction (12 g.), b. p. 130—140°/15 mm., which on redistillation gave the impure *alcohol*, b. p. 129—131°/12 mm., as a colourless mobile oil (Found: C, 80·1; H, 8·8.  $C_{11}H_{14}O$  requires C, 81·5; H, 8·6%). The *phenylurethane*, m. p. 105—106°, crystallises from light petroleum in clusters of colourless fine needles (Found: C, 77·0; H, 6·8.  $C_{18}H_{19}O_2N$  requires C, 76·9; H, 6·8%).

*2:4-Dimethylcinnamyl Alcohol*,  $C_6H_3Me_2\cdot CH:CH\cdot CH_2\cdot OH$ .—A mixture of *α-m-4*-xylylallyl alcohol (8 g.) and acetic anhydride (10 c.c.) was boiled for 6 hours and then fractionated. The 2:4-dimethylcinnamyl acetate, b. p. 168—170°/17 mm., obtained was hydrolysed with a slight excess of 5% alcoholic potassium hydroxide solution, giving 2:4-dimethylcinnamyl alcohol, which was obtained as a pleasant-smelling, straw-coloured, viscous liquid, b. p. 162—164°/19 mm. (Found: C, 80·8; H, 8·6.  $C_{11}H_{14}O$  requires C, 81·5; H, 8·6%). The *phenylurethane* separated from light petroleum in colourless needles, m. p. 82—83° (Found: C, 77·0; H, 6·9.  $C_{18}H_{19}O_2N$  requires C, 76·9; H, 6·8%).

The author is indebted to Professor C. K. Ingold, F.R.S., for his interest in this work and to Mr. A. Rumfitt for carrying out the majority of the analyses recorded. The cost has been partly defrayed with a grant from the Government Grant Committee of the Royal Society, to whom the author's thanks are due.

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## XXXVII.—Some Trinitroethylbenzenes.

By JAMES NELSON EDMUND DAY.

AN account is here given of the preparation of 3:4:5-, 2:3:4-, and 2:4:5-trinitroethylbenzenes, together with some of their reactions. One of the difficulties in the study of derivatives of

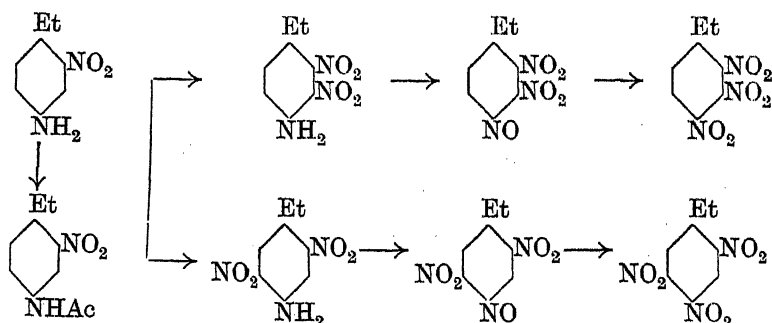


ethylbenzene has been a suitable initial material of undoubted purity; this has been overcome by using *p*-aminoethylbenzene, prepared from pure *p*-aminoacetophenone by the reduction method of Clemmensen (*Ber.*, 1913, 46, 1837; 1914, 47, 51, 681).

On acetylation of *p*-aminoethylbenzene the acetyl derivative described by Paucksch (*Ber.*, 1884, 17, 769) was obtained, and this on nitration gave 3:5-dinitro-4-acetamidoethylbenzene (m. p. 182—183°) identical with that previously described (Paucksch, *loc. cit.*; Brady, Day, and Allam, J., 1928, 982). These experiments were carried out to make certain that the compound described by Paucksch was the *p*- and not the *o*-amino-compound, as it was obtained by separation of the *o*- and *p*-acetamidoethylbenzenes by crystallisation, a process which it had been found difficult to repeat satisfactorily.

3:5-Dinitro-4-aminoethylbenzene, on diazotisation and treatment with sodium nitrite and copper sulphate, gave 3:4:5-trinitroethylbenzene.

*p*-Aminoethylbenzene, on nitration in presence of excess of sulphuric acid, gave 2-nitro-4-aminoethylbenzene identical with the compound prepared by reduction of crude 2:4-dinitroethylbenzene (compare Cline and Read, *J. Amer. Chem. Soc.*, 1927, 49, 3150, who have shown that some 4-nitro-2-aminoethylbenzene is also produced in this reaction; compare also Brady, Day, and Allam, *loc. cit.*). Nitration of 2-nitro-4-acetamidoethylbenzene gave a mixture of 2:3-dinitro- and 2:5-dinitro-4-aminoethylbenzenes which on oxidation with Caro's acid gave respectively 2:3-dinitro-4-nitrosoethylbenzene and 2:5-dinitro-4-nitrosoethylbenzene. Oxidation of the latter compounds with nitric acid gave the required 2:3:4- and 2:4:5-trinitroethylbenzenes.



2:3:4-Trinitroethylbenzene has also been prepared by the direct nitration of 2:3-dinitroethylbenzene.

These trinitroethylbenzenes are very similar to the corresponding

trinitrotoluenes, but their melting points are lower. They form well-defined *methylamine* and *hydrazine* derivatives by replacement of the mobile nitro-group. Their alcoholic solutions give colorations with dilute sodium hydroxide solution. 2:3:4-Trinitroethylbenzene gives a bright green-yellow colour, changing to brown and brownish-red; the corresponding trinitrotoluene gives a green and then a brown colour. 2:4:5-Trinitroethylbenzene gives a bright green, changing to dark green and red; the corresponding trinitrotoluene gives blue, green, and then brown colours. 3:4:5-Trinitroethylbenzene and the corresponding trinitrotoluene both give a bright pink colour, changing to brown.

#### EXPERIMENTAL.

*p-Aminoethylbenzene*.—A mixture of granulated zinc (100 g., left in contact with mercuric chloride, 20 g., in water, 400 c.c., for 12 hours and then washed with water), concentrated hydrochloric acid (200 c.c.), and water (200 c.c.) was gently heated while *p*-aminoacetophenone (25 g.), dissolved in concentrated hydrochloric acid (200 c.c.), was added slowly through an upright condenser, followed by concentrated hydrochloric acid (100 c.c.). After being heated for 5 hours, the mixture was cooled and, a slight excess of a concentrated solution of sodium hydroxide having been added, submitted to steam distillation. The *p*-aminoethylbenzene was extracted from the distillate with ether (average yield, 19.5%; varying the time of boiling or the amount of hydrochloric acid did not greatly affect the yield).

On acetylation with acetic anhydride, the amine gave *p*-acet-amidoethylbenzene, identified by its m. p. and mixed m. p. with a specimen prepared from ethylbenzene.

On nitration with ten times its weight of nitric acid (*d* 1.5), the acetyl compound gave 3:5-dinitro-4-acetamidoethylbenzene, m. p. 182—183° after crystallisation from alcohol. Addition of this substance did not lower the melting point of the 3:5-dinitroacet-amidoethylbenzene previously prepared (Brady, Day, and Allam, *loc. cit.*). This experiment supplied the direct evidence required, that the amino-group in the dinitroacetamidoethylbenzene, m. p. 183°, previously isolated from the nitrated mixture of *o*- and *p*-acet-amidoethylbenzenes, was in the 4-position.

3:4:5-Trinitroethylbenzene.—Sulphur dioxide was passed into nitric acid (*d* 1.5) (5.7 g.) at 0° until the gain in weight was 0.6 g. The solution was cooled to — 12°, 3:5-dinitro-4-aminoethylbenzene (1.4 g.) dissolved in it, the solution poured on ice (20 g.), and the whole added to a mixture of copper sulphate (5.7 g.) and sodium nitrite (1.6 g.) in water (25 c.c.) containing ice (50 g.). After 12

hours, the precipitate was collected, washed, and heated with nitric acid ( $d$  1.42) on the water-bath for 30 minutes, the mixture cooled and diluted, and the product crystallised from nitric acid ( $d$  1.42). A final crystallisation from alcohol containing a little acetic acid gave 3:4:5-*trinitroethylbenzene* in white needles, m. p. 92.5° (Found: C, 39.8; H, 2.9; N, 17.3.  $C_8H_7O_6N_3$  requires C, 39.8; H, 2.9; N, 17.4%).

3:4:5-Trinitroethylbenzene (0.2 g.) in alcohol (6 c.c.) was warmed with 33% methylamine solution (0.3 g.) in alcohol (2 c.c.) on the water-bath for 5 minutes, and the solution diluted with an equal volume of water and cooled. Crystallisation of the precipitate from dilute alcohol gave 3:5-dinitro-4-methylaminoethylbenzene in orange needles, m. p. 73° (Found: C, 47.9; H, 5.0.  $C_9H_{11}O_4N_3$  requires C, 48.0; H, 4.9%).

Similarly, from 3:4:5-trinitroethylbenzene (0.2 g.) in alcohol (6 c.c.) and 50% hydrazine hydrate solution (0.2 g.) in alcohol (4 c.c.), 3:5-dinitro-4-hydrazinoethylbenzene was obtained; it formed copper-red plates, m. p. 85°, on crystallisation from alcohol (Found: C, 42.5; H, 4.5.  $C_8H_{10}O_4N_4$  requires C, 42.5; H, 4.5%).

2-Nitro-4-aminoethylbenzene.—Sulphuric acid ( $d$  1.84) (55 c.c.) was cooled to 0°, and *p*-aminoethylbenzene (5 g.) added slowly. The solution was cooled to -8°, and stirred while a mixture of nitric acid ( $d$  1.5) (3.3 g.) and sulphuric acid ( $d$  1.84) (8 c.c.) was added drop by drop. After being kept at 0° for 30 minutes, the mixture was poured on ice. The precipitated sulphate was decomposed with 2*N*-sodium hydroxide, and the amine extracted with ether. Crystallised from light petroleum, the product melted at the same temperature (45°) as the compound described by Cline and Read (*loc. cit.*).

2:3-Dinitro-4-nitrosoethylbenzene.—2:3-Dinitro-4-aminoethylbenzene (1.58 g.) (Brady, Day, and Allam, *loc. cit.*) was dissolved in sulphuric acid ( $d$  1.84) (5 c.c.) at 0°. Sulphuric acid ( $d$  1.84) (5 c.c.) was cooled in a freezing mixture, finely powdered ammonium persulphate (5.13 g.) added in small quantities at a time, and the solution kept at 0° for an hour and then poured on ice (12 g.) in a stoppered bottle. The sulphuric acid solution of the amine was added, and the mixture shaken occasionally during the following 5 days. The precipitate, after being washed with water and crystallised from alcohol, gave 2:3-dinitro-4-nitrosoethylbenzene in fine yellow crystals, which melted at 80–81° to a dark green liquid (Found: N, 18.5.  $C_8H_7O_5N_3$  requires N, 18.7%). The dark green hot alcoholic solution of this compound became yellow on cooling.

2:3:4-Trinitroethylbenzene.—2:3-Dinitro-4-nitrosoethylbenzene was heated on the water-bath for 30 minutes with an excess of

nitric acid (*d* 1.42), the solution diluted, and the precipitate crystallised from benzene–light petroleum, 2 : 3 : 4-*trinitroethylbenzene* being obtained in pale yellow plates, m. p. 80° (Found : C, 39.7; H, 2.9; N, 17.2.  $C_8H_7O_6N_3$  requires C, 39.8; H, 2.9; N, 17.4%). This compound was also obtained by adding 2 : 3-dinitroethylbenzene (1 g.) slowly to a mixture of nitric acid (*d* 1.5) (1 g.) and sulphuric acid (*d* 1.84) (12 c.c.) and heating the whole at 100° for 2 hours; it separated on cooling and was crystallised as before.

Treated with methylamine as was 3 : 4 : 5-trinitroethylbenzene, it gave 2 : 4-dinitro-3-methylaminoethylbenzene, which crystallised from dilute alcohol in yellow plates, m. p. 92–93° (Found : C, 48.2; H, 4.8.  $C_9H_{11}O_4N_3$  requires C, 48.0; H, 4.9%).

Treated with hydrazine hydrate as described above, it gave 2 : 4-dinitro-3-hydrazinoethylbenzene, which separated from alcohol in bright orange-red needles, m. p. 149° (Found : C, 42.5; H, 4.5.  $C_8H_{10}O_4N_4$  requires C, 42.5; H, 4.5%).

2 : 5-Dinitro-4-nitrosoethylbenzene.—2 : 5-Dinitro-4-aminoethylbenzene (Brady, Day, and Allam, *loc. cit.*) was oxidised with persulphuric acid in the same way as 2 : 3-dinitro-4-aminoethylbenzene. The precipitate was collected after 4 days and crystallised from alcohol, 2 : 5-dinitro-4-nitrosoethylbenzene being obtained in small, deep yellow prisms, m. p. 111–112° (Found : N, 18.4.  $C_8H_7O_5N_3$  requires N, 18.7%). The hot alcoholic solution was dark yellowish-green and the pure substance melted to a dark green liquid.

2 : 4 : 5-Trinitroethylbenzene.—2 : 5-Dinitro-4-nitrosoethylbenzene, on oxidation with nitric acid (*d* 1.42), gave 2 : 4 : 5-trinitroethylbenzene, which separated from benzene–light petroleum in light yellow crystals, m. p. 40° (Found : C, 40.0; H, 3.0; N, 17.6.  $C_8H_7O_6N_3$  requires C, 39.8; H, 2.9; N, 17.4%).

With methylamine, it gave 2 : 4-dinitro-5-methylaminoethylbenzene, which crystallised from alcohol in yellow needles, m. p. 149° (Found : C, 48.2; H, 5.0.  $C_9H_{11}O_4N_3$  requires C, 48.0; H, 4.9%). With hydrazine, it gave 2 : 4-dinitro-5-hydrazinoethylbenzene, which crystallised from alcohol in yellow-brown needles, m. p. 141° (Found : C, 42.7; H, 4.6.  $C_8H_{10}O_4N_4$  requires C, 42.5; H, 4.5%).

The author wishes to thank Dr. O. L. Brady for his interest in this work.

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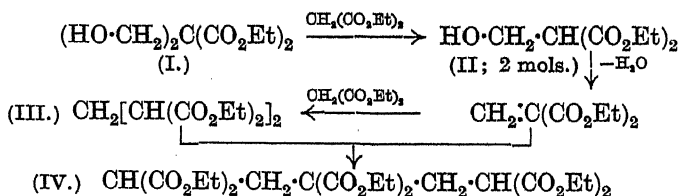
XXXVIII.—*The Reactions of Malonic Esters with Formaldehyde. Part I.*

By KENNETH NORMAN WELCH.

DURING the course of a research requiring large quantities of ethyl methylenedimalonate, it was found that the product prepared by Knoevenagel's method (*Ber.*, 1894, **27**, 2345) varied considerably in yield and contained a substance which decomposed with evolution of formaldehyde during distillation. Although Gault (*Bull. Soc. chim.*, 1912, [iv], **11**, 381) showed that better yields could be obtained by employing an excess of ethyl malonate, it was felt that a more thorough investigation of the reaction would be justified.

Ethyl malonate condenses with formaldehyde in the presence of dilute sodium hydroxide solution to give a solid addition compound, *ethyl di(hydroxymethyl)malonate* (I). The presence of two hydroxyl groups was proved by the preparation of a *diphenylcarbamate* and a neutral *sulphite*. Further, the ester (I) was converted into  $\alpha$ -iodomethylacrylic acid,  $\text{CH}_2\text{:C}(\text{CH}_2\text{I})\cdot\text{CO}_2\text{H}$ , by the action of hydriodic acid, and this unsaturated acid, which gave the iodoform reaction, was reduced to isobutyric acid by the action of hydriodic acid and red phosphorus. The readiness with which ethyl di(hydroxymethyl)malonate loses formaldehyde forms an interesting comment on a paper by Earl, Ellsworth, Jones, and Kenner (*J.*, 1928, 2697).

When formaldehyde was condensed with a larger excess of ethyl malonate in the presence of dilute sodium hydroxide solution, a saturated compound, probably ethyl hydroxymethylmalonate (II), was produced as an oil: this could not be distilled owing to the ease with which it lost water to give ethyl methylenemalonate. This substance is responsible for the more complex condensation products obtained by the action of formaldehyde on ethyl malonate: the production of ethyl methylenedimalonate (III) and ethyl pentane- $\alpha\alpha\gamma\gamma\gamma$ -hexacarboxylate (IV) (compare Bottomley and Perkin, *J.*, 1900, **77**, 294) is explained as follows:



The above reactions take place independently under the conditions employed in the condensation of formaldehyde and ethyl malonate.

For instance, ethyl di(hydroxymethyl)malonate reacts with ethyl malonate in the presence of piperidine, triethylamine, or potassium hydroxide (*a*; p. 260) to give a mixture of (III) and (IV), and the yield of the latter is decreased when a larger excess of ethyl malonate is used (*b*; p. 260): experiment (*c*) (p. 260) shows that the last result is not due to the action of ethyl malonate on (IV). Further, ethyl methylenemalonate condenses readily with ethyl malonate and with ethyl methylenedimalonate (III) in the presence of piperidine to give (III) and (IV) respectively.

Although ethyl hydroxymethylmalonate (II) is incapable of isolation in the pure state, its alkyl substitution products, for example, *ethyl (hydroxymethyl)ethylmalonate*, can be distilled in a vacuum without decomposition.\* This ester reacts with ethyl malonate in the presence of piperidine to give ethyl methylenedimalonate and ethyl ethylmalonate, but no facile reaction occurs between ethyl (hydroxymethyl)ethylmalonate and ethyl ethylmalonate.

#### EXPERIMENTAL.

*Ethyl Di(hydroxymethyl)malonate* (I).—Ethyl malonate (100 g.), 40% formalin (180 g.), and a few drops of B.D.H. Universal Indicator were mixed and 10% sodium hydroxide solution was gradually added. Reaction began at  $p_H$  7.5 and was rapid at  $p_H$  8.5. Owing to slight hydrolysis of the ester the  $p_H$  was apt to fall, and sodium hydroxide was added during 48 hours to maintain it between 8 and 9. The mixture became homogeneous and the temperature was kept below 50°. The mixture was then diluted with water (2 vols.), shaken with the smallest quantity of ether necessary to remove insoluble impurities, saturated with sodium chloride, and extracted five times with ether. The dried extracts, on removal of the ether, left a residue, which was heated in a vacuum at 50–60°. The glycerol-like substance remaining solidified after some months or more quickly on generous seeding. After being drained on porous plate and recrystallised from benzene–petroleum (b. p. 100–120°) or, better, from ether–amyl ether, *ethyl di(hydroxymethyl)malonate* was obtained in colourless elongated prisms, m. p. 52–53° (Found: C, 49.1, 48.9; H, 7.1, 7.2; OEt, 40.1.  $C_9H_{16}O_6$  requires C, 49.1; H, 7.3; OEt, 40.9%). This ester has an intensely bitter taste and is very soluble in water, alcohol, ether, and benzene and slightly soluble in light petroleum and amyl ether. It is decomposed by heat into formaldehyde, water, alcohol, carbon dioxide, small

\* Such condensations appear to be general and experiments with formaldehyde and ethyl butane- $\alpha\beta$ -tricarboxylate are in progress with a view to the synthesis of pilocarpic acid (Jowett, J., 1901, 79, 1331).

quantities of ethyl acrylate and ethyl methylenemalonate and a large quantity of high-boiling tar.

The *diphenylcarbamate*, prepared by the action of phenylcarbamide (5 g.) on ethyl di(hydroxymethyl)malonate (5 g.) during one week at the room temperature, crystallised from alcohol in needles (8 g.), m. p. 161° (Found: C, 60.0; H, 5.8; N, 6.3.  $C_{23}H_{26}O_8N_2$  requires C, 60.3; H, 5.7; N, 6.1%). *Ethyl di(hydroxymethyl)malonate sulphite*, prepared by the action of thionyl chloride (11.8 g.) on ethyl di(hydroxymethyl)malonate (22 g.) in anhydrous ether for 6 hours, distilled as a colourless oil (19 g.), b. p. 166°/20 mm. (Found: C, 40.6; H, 5.3.  $C_9H_{14}O_7S$  requires C, 40.6; H, 5.2%).

*$\alpha$ -Iodomethylacrylic Acid*.—Ethyl di(hydroxymethyl)malonate (10 g.) and hydriodic acid (*d* 1.71; 66 g.) were boiled for 45 minutes, ethyl iodide and carbon dioxide being evolved. After cooling and standing for 1 hour, the solid (7 g., m. p. 95–100°) was collected, washed with a little water, and rapidly recrystallised from boiling water; it separated in cream-coloured plates, m. p. 104–106° (slight decomp.). A somewhat purer specimen (m. p. 106–107°) of the same substance was obtained by subjecting ethyl di(hydroxymethyl)malonate to a preliminary hydrolysis with 3% sulphuric acid at 120–140°, and treating the crude acid (which rapidly polymerises) with cold hydriodic acid (Found: C, 22.6; H, 2.4; *M*, ebullioscopic in ether, 220.  $C_4H_5O_2I$  requires C, 22.6; H, 2.4%; *M*, 212).  *$\alpha$ -Iodomethylacrylic acid* rapidly turns brown on exposure to light and air.

*Reduction of  $\alpha$ -Iodomethylacrylic Acid*.—Ethyl di(hydroxymethyl)malonate (25 g.) was converted into iodomethylacrylic acid by heating with hydriodic acid as described above. Red phosphorus (7 g.) and hydriodic acid (30 g.) were then added and the mixture was boiled for 10 hours. After dilution with an equal volume of water, the mixture was steam-distilled; the distillate was neutralised with sodium hydroxide and evaporated to dryness. Excess of 50% sulphuric acid was added; the liberated acid, isolated by extraction with ether, boiled at 150–160°. It was converted into the chloride by the action of the theoretical quantity of boiling thionyl chloride for 20 minutes, and the product poured into an excess of aniline (6 g.). After being heated on the water-bath for 20 minutes, the product was poured into an excess of dilute hydrochloric acid; the solid obtained, after recrystallisation from dilute alcohol, melted at 103–105°, alone or in admixture with authentic isobutyranilide.

*Ethyl (Hydroxymethyl)malonate (II)*.—Formalin (10 g.), ethyl malonate (60 g.), and enough alcohol to give a homogeneous mixture were mixed with a few drops of B.D.H. Universal Indicator, and

sodium hydroxide solution added to produce  $p_H$  9. After 24 hours, the mixture was rendered faintly acid, diluted with water, and extracted with ether. After drying and removal of the solvent, the excess of ethyl malonate was distilled off in a vacuum, leaving ethyl (hydroxymethyl)malonate as an oil, which was almost without action on dilute potassium permanganate solution. Treated with phenylcarbimide, the ester gave diphenylurea, m. p.  $238^\circ$ .

*Condensation of Ethyl Di(hydroxymethyl)malonate with Ethyl Malonate.*—(a) Ethyl di(hydroxymethyl)malonate (10 g.), ethyl malonate (20 g.), and piperidine, triethylamine or alcoholic potassium hydroxide (a few drops) were heated for 6 hours in the water-bath. On cooling and standing over-night, crystals separated. The whole was then fractionated, giving: (i) ethyl methylenedimalonate (10 g.), b. p.  $140\text{--}180^\circ/5$  mm., which on hydrolysis gave glutaric acid, m. p.  $95\text{--}97^\circ$ , not depressed by admixture with an authentic specimen; (ii) ethyl pentane- $\alpha\gamma\gamma\gamma$ -hexacarboxylate (10 g.), b. p.  $180\text{--}240^\circ/5$  mm., which solidified and, after being drained and recrystallised from alcohol, melted at  $52\text{--}53^\circ$  (Found: C, 54.9; H, 7.0. Calc. for  $C_{23}H_{36}O_{12}$ : C, 54.8; H, 7.1%).

(b) A similar experiment with 60 g. of ethyl malonate instead of 20 g. yielded ethyl methylenedimalonate (27 g.) but no pentane derivative (IV).

(c) The condensation (a) was repeated, but, after the preliminary heating, the product was mixed with ethyl malonate (35 g.) and a few drops of piperidine and heated for a further 6 hours. Ethyl pentane- $\alpha\gamma\gamma\gamma$ -hexacarboxylate (10 g.) was isolated after removal of the excess of ethyl malonate.

*Ethyl (hydroxymethyl)ethylmalonate*, prepared by condensing ethyl ethylmalonate (20 g.) and formalin (30 g.) for 48 hours under the conditions employed for the condensation of formalin with ethyl malonate, was obtained as an oil (15 g.), b. p.  $105\text{--}107^\circ/4$  mm. (Found: C, 54.8; H, 8.3.  $C_{10}H_{18}O_5$  requires C, 55.0; H, 8.3%). The *phenylcarbamate* crystallised from dilute methyl alcohol in plates, m. p.  $63\text{--}64^\circ$  (Found: C, 60.5; H, 6.9.  $C_{17}H_{23}O_5N$  requires C, 60.5; H, 6.8%).

Ethyl (hydroxymethyl)ethylmalonate (2 g.), ethyl malonate (5 g.), and piperidine (1 drop) were heated on the water-bath for 5 days. Distillation then yielded ethyl ethylmalonate, b. p.  $90\text{--}100^\circ/12$  mm., and ethyl methylenedimalonate, b. p.  $190\text{--}200^\circ/12$  mm., which was hydrolysed to glutaric acid, m. p.  $94\text{--}96^\circ$ .

No apparent reaction took place on the water-bath between ethyl (hydroxymethyl)ethylmalonate and ethyl ethylmalonate in the presence of piperidine. At  $130\text{--}140^\circ$ , alcohol was eliminated, but nothing further could be isolated from the product.



*Condensation of Ethyl Methylenemalonate with Ethyl Malonate and with Ethyl Methylenedimalonate.*—Ethyl methylenemalonate (freshly distilled) (2 g.) and ethyl malonate were mixed and methyl-alcoholic potassium hydroxide (1 drop) was added; considerable heat was evolved. After standing in the cold for 1 hour, the product was unreactive to dilute potassium permanganate solution and on distillation gave ethyl methylenedimalonate (3 g.), as proved by conversion into glutaric acid.

Under the same conditions, the condensation with ethyl methylenedimalonate was complete after 1 hour's heating on the water-bath; the mixture solidified on cooling and was proved to be ethyl pentane- $\alpha\alpha\gamma\gamma$ -hexacarboxylate by the mixed m. p. method.

The author wishes to thank the Chemical Society for a grant which has partly defrayed the cost of the materials used in this research.

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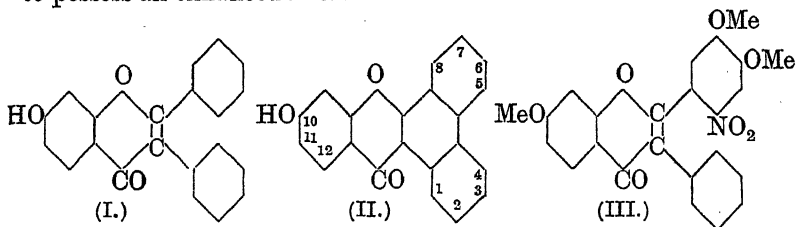
### XXXIX.—*Colloidal Phenoxides. Part II. Some Phenanthraxanthones.*

By WILSON BAKER.

A NUMBER of derivatives of 7-hydroxybenzo- $\gamma$ -pyrone containing aromatic groups in positions 2 and 3 dissolve in hot aqueous alkaline solutions and yield gels on cooling. The relationships existing between the chemical constitution and the capability of forming gels in these compounds was established in Part I (Baker and Eastwood, J., 1929, 2897), and the ultimate object of the work was indicated. Briefly, this was to prepare a substance which should give a gel in alkaline solutions and at the same time exhibit fluorescence, so that by examination in ultra-violet light the structure of the gel might be visible.

The simplest derivative of benzo- $\gamma$ -pyrone which gives a gel is 7-hydroxy-2:3-diphenylbenzo- $\gamma$ -pyrone (I), and the attempt to make the molecule fluoresce while retaining the colloidal properties is described in this paper. The work recorded in Part I showed that only minor changes could be made in the molecule (I) without destroying the desired physical properties of the alkali salts. Such changes as can be made within these limitations consist of alteration of the substituents in positions 2 and 3 (introduction of a *p*-methoxy-group, replacement of phenyl by styryl) and the intro-

duction of a further hydroxyl group in position 5. No such changes can be expected, nor are found, to increase appreciably the fluorescence of the substance (I), and it was obvious that some other type of simple alteration to the molecule was necessary. Attention was therefore directed to the synthesis of 10-hydroxyphenanthraxanthone\* (II), in which the two phenyl nuclei are united, so that the substance, being a phenanthrene derivative, might be expected to possess an enhanced fluorescence.

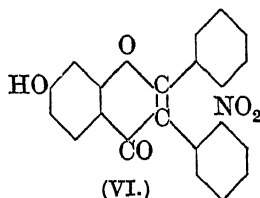
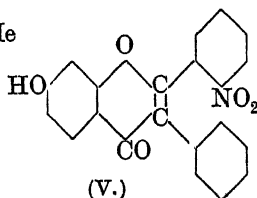
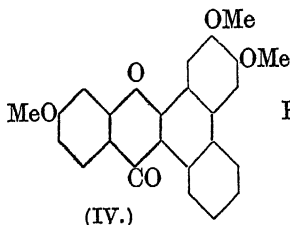


This synthesis has now been achieved, but both the physical and the optical properties of the alkali salts of the substance are such that it is very doubtful if it will serve the purpose for which it was intended. The gels are unstable and without appreciable fluorescence.

The ring closure between the two phenyl nuclei was effected by means of Pschorr's phenanthrene synthesis, and in order to study the conditions of the reaction use was made of the readily accessible 7-methoxy-3-phenyl-2-(6-nitro-3:4-dimethoxyphenyl)benzo- $\gamma$ -pyrone (III). This substance was prepared by the nitration of 7-methoxy-3-phenyl-2-(3:4-dimethoxyphenyl)benzo- $\gamma$ -pyrone (Part I, *loc. cit.*) in acetic acid solution, the position of the nitro-group being inferred from the great reactivity of the veratryl nucleus in position 6, and the success of the subsequent ring closure. Reduction with tin and hydrochloric acid gave 7-methoxy-3-phenyl-2-(6-amino-3:4-dimethoxyphenyl)benzo- $\gamma$ -pyrone, and a methyl-alcoholic solution of the sulphate of this base, when diazotised and subsequently boiled, deposited the very sparingly soluble 6:7:10-trimethoxyphenanthraxanthone (IV) in 70% yield. This compound was demethylated by boiling with hydrobromic acid and acetic acid, giving 6:7:10-trihydroxyphenanthraxanthone. The high yield of (IV) is doubtless to be attributed to the spatial arrangement of the *o*-nitrophenyl and

\* At the suggestion of the Editor the parent substance has received the name "phenanthraxanthone" with the numbering shown. The formula (II) should be inverted, but in order not to confuse the relation of the substance to the diphenylbenzo- $\gamma$ -pyrone from which it is prepared, the representation above is adopted in this paper.

the phenyl group, *cis-trans* isomerism about the ethylenic linkage being impossible.



The synthesis of (II) was effected as follows. When 2:4-dihydroxyphenyl benzyl ketone was heated under carefully defined conditions with *o*-nitrobenzoic anhydride and sodium *o*-nitrobenzoate and the product was hydrolysed with alcoholic potassium hydroxide, 7-hydroxy-3-phenyl-2-*o*-nitrophenylbenzo- $\gamma$ -pyrone (V) was obtained. The methyl ether of this compound was reduced with tin and hydrochloric acid to the base 7-methoxy-3-phenyl-2-*o*-aminophenylbenzo- $\gamma$ -pyrone, and diazotisation of this substance in the manner described above yielded 10-methoxyphenanthraxanthone, from which 10-hydroxyphenanthraxanthone (II) was obtained by demethylation with hydrobromic acid in acetic acid.

Owing to difficulties encountered in the preparation of (V), the synthesis of (II) was attempted in another way. *o*-Nitrophenylacetonitrile was condensed with resorcinol under the conditions of the Hoesch reaction, giving 2:4-dihydroxyphenyl *o*-nitrobenzyl ketone; this, when heated with benzoic anhydride and sodium benzoate, yielded a product which gave 7-hydroxy-2-phenyl-3-*o*-nitrophenylbenzo- $\gamma$ -pyrone (VI) on hydrolysis. The corresponding methyl ether, however, when reduced with tin and hydrochloric acid or with ferrous sulphate and ammonia, yielded, not a primary base, but an uncrystallisable substance showing some of the properties of a secondary amine. It is possible that ring closure may occur between the amino-group first produced and the carbonyl group, and that further reduction then takes place.

#### EXPERIMENTAL.

7-Methoxy-3-phenyl-2-(6-nitro-3:4-dimethoxyphenyl)benzo- $\gamma$ -pyrone (III).—7-Hydroxy-3-phenyl-2-(3:4-dimethoxyphenyl)benzo- $\gamma$ -pyrone (Part I, *loc. cit.*) (10 g.) was dissolved in warm glacial acetic acid (75 c.c.), and to the cooled solution was added a mixture of glacial acetic acid (50 c.c.) and concentrated nitric acid (50 c.c.; *d* 1.42). After 2 hours, the red solution was poured into water, and the precipitated nitro-compound collected; it crystallised from

alcohol, in which it was sparingly soluble, in light yellow, thick, diamond-shaped plates (or hexagonal plates), m. p.  $222^{\circ}$  (Found : C, 66.0; H, 4.6; N, 3.5.  $C_{24}H_{19}O_7N$  requires C, 66.5; H, 4.4; N, 3.2%). In contrast to the unnitrated substance, this compound shows no basic properties towards hydrochloric acid.

*7-Methoxy-3-phenyl-2-(6-amino-3:4-dimethoxyphenyl)benzo- $\gamma$ -pyrone.*—The finely powdered nitro-compound (III) (10 g.), alcohol (300 c.c.), finely divided granulated tin (25 g.), and concentrated hydrochloric acid (60 c.c.) were gently boiled for 6 hours; alcohol (100 c.c.) was then removed by distillation. The filtered solution deposited thick, hexagonal, light yellow plates of the *stannichloride*, which were collected after 12 hours and washed with a little alcohol (yield, 8.7 g.). The substance slowly darkens from  $200^{\circ}$  and melts with decomposition at about  $240^{\circ}$  [Found : C, 49.6; H, 4.2.  $(C_{24}H_{19}O_5NH_2, HCl)_2SnCl_4$  requires C, 50.5; H, 3.9%]. The *stannichloride* (2.5 g.) was dissolved in hot 50% alcohol (50 c.c.) containing concentrated hydrochloric acid (1 c.c.) and a rapid stream of hydrogen sulphide was passed through the hot solution. When the filtered, tin-free liquid was treated with an excess of concentrated aqueous ammonia, the free *amino*-compound separated in small, sulphur-yellow, diamond-shaped plates, m. p.  $208^{\circ}$  (Found : C, 71.3; H, 5.4; N, 3.7.  $C_{24}H_{21}O_5N$  requires C, 71.4; H, 5.3; N, 3.5%). Yield, 7 g. from 10 g. of the nitro-compound. The *hydrochloride* separates from 50% alcoholic hydrochloric acid in very pale yellow, hexagonal plates (Found : N, 3.2; Cl, 7.7.  $C_{24}H_{21}O_5N, HCl$  requires N, 3.2; Cl, 8.1%). It slowly becomes more yellow at  $100^{\circ}$  owing to loss of hydrogen chloride; the same change takes place on heating with water or organic solvents or in a vacuum over sodium hydroxide.

*6:7:10-Trimethoxyphenanthraxanthone* (IV).—The preceding *amino*-compound (1 g.) was dissolved in a warm mixture of methyl alcohol (120 c.c.) and concentrated sulphuric acid (2 g.) and cooled to  $-10^{\circ}$ . A 5% aqueous solution of sodium nitrite (13.9 c.c.) was then added during  $\frac{1}{2}$  hour, and the solution subsequently kept at  $0^{\circ}$  for 2 days. The liquid, which now contained a small amount of crystalline material, was boiled under reflux for  $\frac{1}{2}$  hour, colourless needles being deposited. These were separated from the hot liquid by filtration, washed with much alcohol and with water, and dried (yield, 0.7 g.); m. p.  $232-233^{\circ}$  (Found : C, 74.3; H, 4.8.  $C_{24}H_{18}O_5$  requires C, 74.6; H, 4.7%). *6:7:10-Trimethoxyphenanthraxanthone* is almost insoluble in most organic solvents. It separates from a large volume of boiling glacial acetic acid in hair-like needles. It dissolves in concentrated sulphuric acid to an orange-yellow solution which exhibits no fluorescence, and

shows feebly basic properties towards concentrated hydrochloric acid.

6:7:10-*Trihydroxyphenanthraxanthone*.—The attempted demethylation of the trimethoxyphenanthraxanthone (IV) with hydriodic acid, or hydriodic acid in acetic acid, was unsatisfactory, owing to the precipitation of an insoluble dark-green hydriodide of the methylated compound.

6:7:10-Trimethoxyphenanthraxanthone (0.5 g.) was boiled with glacial acetic acid (25 c.c.) and hydrobromic acid (25 c.c.;  $d$  1.5) for 8 hours. After  $2\frac{1}{2}$  hours, the solution began to deposit orange crystals of a hydrobromide, which gradually increased in amount, and were finally collected and washed with very dilute sodium bicarbonate solution and with water; the free trihydroxyphenanthraxanthone was then obtained as a pale yellow powder. By dissolving it in a large volume of boiling alcohol and filtering and concentrating the solution, it was obtained in small blunt-ended prisms, which when rapidly heated melted at  $318\text{--}319^\circ$  with much darkening. The substance contains alcohol of crystallisation which is lost at  $110^\circ$ , the crystals becoming opaque (Found: C, 70.9; H, 5.3. Found in material dried at  $110^\circ$ : C, 72.9; H, 3.9.  $C_{21}H_{12}O_5 \cdot EtOH$  requires C, 70.8; H, 4.7%.  $C_{21}H_{12}O_5$  requires C, 73.3; H, 3.5%). 6:7:10-*Trihydroxyphenanthraxanthone* as a xanthone derivative with vicinal hydroxyl groups is a weak mordant dye. On cotton mordanted with iron, aluminium and tin, it gives greyish-brown, pale lemon-yellow, and bright yellow shades respectively. Its alcoholic solution develops an intense dull bluish-green colour with ferric chloride.

*o*-Nitrobenzoic Anhydride.—This was prepared by a modification of the method of D.R.-P. 201325 (compare Robinson and Venkataraman, J., 1929, 63). *o*-Nitrobenzoic acid (33.4 g.) was dissolved in a mixture of dry ether (50 c.c.) and pyridine (15.8 g.), and a solution of thionyl chloride (11.9 g.) in ether (50 c.c.) was added with vigorous shaking. After 24 hours, ice and dilute hydrochloric acid were added and the solid product was collected, washed successively with dilute hydrochloric acid, sodium bicarbonate solution, and much water, and dried at first in the air, then at  $100^\circ$ . The anhydride (24 g.) formed a white crystalline powder, m. p.  $126\text{--}128^\circ$ . Bischoff and Rach (*Ber.*, 1884, 17, 2789) state that the substance is explosive, but the author is unable to confirm this. The anhydride can be heated to  $200^\circ$  without decomposition, and when heated as rapidly as possible to very high temperatures in a small tube it decomposes suddenly but without explosion.

7-Hydroxy-3-phenyl-2-*o*-nitrophenylbenzo- $\gamma$ -pyrone (V).—The interaction of *o*-nitrobenzoic anhydride, 2:4-dihydroxyphenyl

benzyl ketone, and sodium *o*-nitrobenzoate under the ordinary conditions of the chromone synthesis ( $180^{\circ}$  for 10 hours) gives a negligible yield of the desired product. After many failures, the following method was found to give fairly satisfactory results and the *o*-nitrobenzoic acid was recoverable.

2:4-Dihydroxyphenyl benzyl ketone (4 g.), *o*-nitrobenzoic anhydride (16 g.), and sodium *o*-nitrobenzoate (4 g.) were heated at  $153^{\circ}$  (anisole vapour bath) for  $2\frac{1}{2}$  hours. The product was dissolved in hot 90% alcohol (60 c.c.) and boiled with potassium hydroxide (8 g.), dissolved in a little water, for 2 minutes. The solution was diluted with water (200 c.c.) and saturated with carbon dioxide and the precipitate was collected, washed, and crystallised from alcohol (charcoal) (yield, 1.1 g.). A further recrystallisation from alcohol yielded pale yellow prisms, m. p.  $268^{\circ}$  (Found: N, 3.9.  $C_{21}H_{13}O_5N$  requires N, 3.9%). The methyl ether, prepared quantitatively by the action of methyl sulphate and alkali upon a 50% acetone-alcohol solution of the compound, crystallised from alcohol in pale yellow, highly refracting, four-sided bi-pyramids, m. p.  $183^{\circ}$  (Found: C, 70.8; H, 4.1.  $C_{22}H_{15}O_5N$  requires C, 70.8; H, 4.1%).

7-Methoxy-3-phenyl-2-*o*-aminophenylbenzo- $\gamma$ -pyrone.—The preceding methyl ether (3.5 g.), alcohol (200 c.c.), granulated tin (20 g.), and concentrated hydrochloric acid (50 c.c.) were boiled for 6 hours. The solution was diluted with water and treated while hot with hydrogen sulphide and the tin-free filtrate was rendered alkaline with excess of ammonia solution and at once filtered from a small amount of flocculent material. The base crystallised completely on further dilution (yield, 3.2 g.); on recrystallisation from alcohol it formed thin, pale-yellow, diamond-shaped plates, m. p.  $213^{\circ}$  (Found: N, 4.4.  $C_{22}H_{17}O_3N$  requires N, 4.1%).

10-Methoxyphenanthraxanthone.—The preceding base (1 g.) was dissolved in warm methyl alcohol (120 c.c.) containing concentrated sulphuric acid (2 g.), cooled to  $-10^{\circ}$ , and diazotised by the gradual addition of 5% aqueous sodium nitrite (10.2 c.c.). The solution was kept for 24 hours at  $0^{\circ}$  and then boiled for  $\frac{1}{2}$  hour and the crystalline precipitate was collected, washed with water and alcohol, and recrystallised from glacial acetic acid, in which it was very sparingly soluble. It separated in very pale yellow prisms, m. p.  $248-249^{\circ}$  (Found: C, 80.8; H, 4.3.  $C_{22}H_{14}O_3$  requires C, 81.0; H, 4.3%). The solution in concentrated sulphuric acid is yellow and slowly develops a strong blue fluorescence.

10-Hydroxyphenanthraxanthone (II).—The preceding compound (0.4 g.) was boiled for 12 hours with glacial acetic acid (60 c.c.) and hydrobromic acid (20 c.c.; *d* 1.5). The product which separated on cooling was collected and acetylated by boiling for 1 hour with acetic

anhydride and a drop of pyridine. The acetyl derivative subsequently separated in colourless prisms, m. p. 234—235°. Hydrolysis of this compound was effected by boiling its alcoholic suspension with a few drops of aqueous sodium hydroxide; a yellow solution exhibiting a weak green fluorescence was then produced. Acidification threw down a gelatinous precipitate, which, after boiling with water, was collected and pressed on porous earthenware. The substance was now dissolved in a large volume of boiling glacial acetic acid (charcoal); after concentration to a small bulk, the solution deposited bunches of fine colourless needles, m. p. 325—326° with slight darkening (Found: C, 80·5; H, 3·9.  $C_{21}H_{12}O_3$  requires C, 80·8; H, 3·9%).

10-Hydroxyphenanthraxanthone dissolves in dilute aqueous sodium hydroxide to a yellow solution which sets to a turbid gel on cooling. The gel has no marked fluorescence and, unlike those described in Part I, is not very stable and shows a great tendency to deposit the alkali salt as a fibrous curd. The solution of 10-hydroxyphenanthraxanthone in concentrated sulphuric acid is yellow and slowly develops a greenish-blue fluorescence.

*o*-Nitrophenylacetonitrile.—*o*-Nitrophenylpyruvic acid was prepared by the modification of Reissert's method (*Ber.*, 1897, 30, 1036) suggested by Gulland and Haworth (*J.*, 1928, 585). The oxime of this acid (Reissert, *Ber.*, 1908, 41, 3813) was readily converted into *o*-nitrophenylacetonitrile by warming it with its own weight of acetic anhydride; a vigorous reaction rapidly occurred, after a few minutes water was added, and the crystalline nitrile, which separated on shaking, was collected, washed, and dried (yield, almost quantitative).

2:4-Dihydroxyphenyl *o*-Nitrobenzyl Ketone.—A mixture of *o*-nitrophenylacetonitrile (10 g.) and resorcinol (20 g.) in anhydrous ether (300 c.c.) was saturated with a rapid stream of hydrogen chloride without external cooling until all had dissolved. Powdered zinc chloride (10 g.) was then added and the solution was cooled to 0° and again saturated with hydrogen chloride. After 48 hours, water was added and the ketimine hydrolysed by heating on the steam-bath for 1 hour. The solid ketone (10·5 g.), which separated on cooling, was used directly for the preparation of the benzo- $\gamma$ -pyrone (VI). The pure substance separates from dilute alcohol (charcoal) in very pale yellow, prismatic needles, m. p. 159—161° (Found: N, 5·2.  $C_{14}H_{11}O_5N$  requires N, 5·1%). Its alcoholic solution gives a deep reddish-brown coloration with ferric chloride. The solution in aqueous sodium hydroxide is yellow.

7-Hydroxy-2-phenyl-3-*o*-nitrophenylbenzo- $\gamma$ -pyrone (VI).—The preceding ketone (10 g.), benzoic anhydride (75 g.), and sodium benzoate

(10 g.) were stirred and heated at 180—190° for 6 hours. The product was dissolved in alcohol (200 c.c.), heated for 20 minutes with potassium hydroxide (40 g.) in water (100 c.c.), diluted with a large volume of water, and saturated with carbon dioxide. The *pyrone* was used without further purification for the preparation of its methyl ether. The pure substance separates from a small amount of alcohol in very pale yellow octahedra, m. p. 267° (Found : N, 4.1.  $C_{21}H_{13}O_5N$  requires N, 3.9%).

The *methyl* ether, prepared in the same manner as the methyl ether of (V), crystallised from alcohol in colourless prismatic needles, m. p. 178° (Found : C, 70.7; H, 3.9.  $C_{22}H_{15}O_5N$  requires C, 70.8; H, 4.0%). The reduction of this compound in the manner described for the reduction of the methyl ether of (V) gave a light yellow powder, which could not be obtained in the crystalline state. The substance, which is very readily soluble in all the common organic solvents except light petroleum, develops a greenish tint on exposure to light, and cannot be diazotised. It gives a weak Liebermann's nitroso-reaction. A similar result was obtained by reduction with ferrous sulphate and ammonia.

The author wishes to record his thanks to Miss F. M. Eastwood, B.A., B.Sc., for carrying out the preliminary experiments with *o*-nitrobenzoic anhydride, and to Dr. J. M. Gulland for advice in connexion with the phenanthrene ring closure.

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OXFORD:

[Received, December 23rd, 1929.]

## XL.—*An Investigation into the Formation of 4(5)-Aminoglyoxalines. Part I.*

By ISIDORE ELKANAH BALABAN.

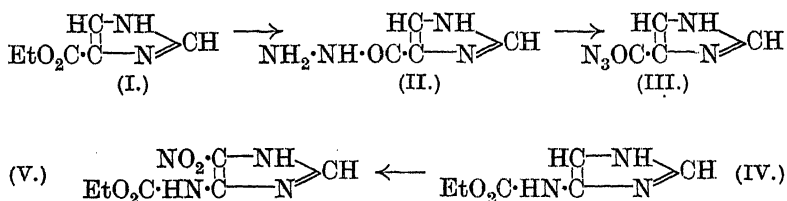
THE only evidence at present (Fargher, J., 1920, **117**, 668; Pyman, J., 1922, **121**, 2616) that 4(5)-aminoglyoxalines are true aromatic amines is the formation, after diazotisation, of coloured solutions with aqueous sodium  $\beta$ -naphthoxide. In order to submit examples of them to typical reactions characteristic of aromatic amines, it seemed desirable to commence a detailed study of their formation and stability. They have hitherto been prepared by the reduction of 4(5)-nitroglyoxalines and 4(5)-benzeneazoglyoxalines (Fargher and Pyman, J., 1919, **115**, 235; Windaus and Langenbeck, *Ber.*, 1923, **56**, 685).

Reduction of 4(5)-nitro-2-methyl- and of 4(5)-nitro-glyoxalines with iron and water (and a drop of acetic acid), ferrous sulphate



and sodium hydroxide, sodium sulphide, or activated aluminium or by West's method, (J., 1925, 127, 494) gave no basic material; the dark blue solutions mentioned by previous workers were, however, often obtained. (Catalytic hydrogenation is under investigation.)

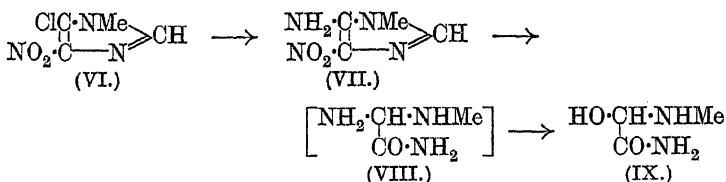
The present communication deals mainly with the application of the Curtius synthesis of amines to ethyl glyoxaline-4(5)-carboxylate (I). When this ester is heated with hydrazine hydrate, *glyoxaline-4(5)-carboxyhydrazide* (II) is obtained, which is converted by treatment with nitrous acid into *glyoxaline-4(5)-carboxyazide* (III): this compound, heated with ethyl alcohol on the water-bath, yields 4(5)-*carbethoxyaminoglyoxaline* (IV). Similarly, with methyl alcohol, the *carbomethoxyamino*-derivative can be prepared.



Attempts to convert the azide by boiling with water into the *s*-carbamide failed: the solution gave an intense Pauly reaction, but an amorphous picrate only could be isolated. The carbomethoxy- and carbethoxy-amino-derivatives were recovered to the extent of about 30% and 50% respectively after boiling with hydrochloric acid, and attempts to obtain 4(5)-aminoglyoxaline by heating them with 2*N*-hydrochloric acid in a sealed tube at 150° or with concentrated sulphuric acid on the water-bath were likewise unsuccessful. Satisfactory hydrolysis also could not be effected with 10% aqueous sodium carbonate or boiling 2*N*-sodium hydroxide. The phthalimido-derivative, which might be quantitatively hydrolysed to the amine (compare Ing and Manske, J., 1926, 2348), could not be prepared. The *as*-carbamide was not formed when the carbethoxyamino-derivative was heated with 3.5% alcoholic ammonia at 150°. 4(5)-*Nitro-5(4)-carbethoxyaminoglyoxaline* (V), notwithstanding the presence of a nitro-group in the *o*-position with respect to the substituted amino-group, also could not be converted by hydrolysis with 10% aqueous sodium carbonate into the corresponding amine.

Balaban and Pyman (J., 1924, 125, 1565) and Sarasin and Wegmann (*Helv. Chim. Acta*, 1924, 7, 713) have shown that the halogen atom in 5-chloro-4-nitro-1-methylglyoxaline (VI) can be replaced by the sulpho- and the cyano-group. The compound does not react with aqueous ammonia or acetamide, but when it is heated

with 3.5% alcoholic ammonia at 140° 4-nitro-5-amino-1-methylglyoxaline (VII) is obtained in good yield. This amine does not form an acetyl or a benzylidene derivative, but after treatment with nitrous acid it gives with alkaline  $\beta$ -naphthol a greenish-blue insoluble dye and with alkaline resorcinol a violet solution, whereas with sodium hydroxide only a pale yellow colour is obtained. The amine is rapidly decomposed by 16% hydrochloric acid (or even 7%) at room temperature, nitrous acid being liberated and a compound, m. p. 140°, formed: this is presumably  $\alpha$ -methylamino- $\alpha$ -hydroxyacetamide (IX), because when it is boiled with aqueous sodium hydroxide it yields ammonia and methylamine. Owing to the



mild conditions of hydrolysis, fission occurs at the 1:2- and the 2:3-positions of (VII), formic acid being split off [compare the formation of dibenzoyldiaminoethylene from glyoxaline (Bamberger and Berle, *Ber.*, 1892, 25, 278) and of *DL*-alanine-*N*-methyldiamidine from 5-amino-1:4-dimethylglyoxaline (Pyman, *loc. cit.*)]. The substance (VIII) is then acted upon by the liberated nitrous acid, hydroxyl being substituted for the amino-group. The formation of glyoxylic acid on alkaline hydrolysis of the amide (IX), and its subsequent conversion into glycollic acid, must be presumed, for the only identifiable acid obtained was oxalic acid. As Böttinger (*Annalen*, 1879, 198, 217) has shown that ammonium  $\alpha$ -amino- $\alpha$ -hydroxyacetate is decomposed by boiling water, the possibility of obtaining the acid corresponding to (IX) and its conversion directly into methylamine and glyoxylic acid was very remote.

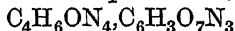
#### EXPERIMENTAL.

For the preparation of glyoxaline-4(5)-carboxylic acid (Fargher and Pyman, *loc. cit.*; Balaban and Pyman, *J.*, 1922, 121, 954) it is unnecessary to isolate the carboxyanilide. After removal of unchanged glyoxaline-4:5-dicarboxylic acid, the acid solution is concentrated to 25 c.c. and treated with concentrated hydrochloric acid (250 c.c.); 50 g. of the dicarboxylic acid give about 20 g. of glyoxaline-4(5)-carboxylic acid.

*Glyoxaline-4(5)-carboxylhydrazide* (II).—When a mixture of 5.6 g. of ethyl glyoxaline-4(5)-carboxylate and hydrazine hydrate (4.0 c.c.; 2 mols.) was heated on the water-bath, solution took place in 15

minutes; after a further 15 minutes, when the solution was cooled, the *hydrazide* (5.0 g.), m. p.  $210^{\circ}$ , separated in almost quantitative yield. It crystallised from boiling water, in which it was fairly readily soluble, in long, colourless, silky needles containing  $1\text{H}_2\text{O}$ , m. p.  $213^{\circ}$  (Found for air-dried substance: loss at  $100^{\circ}$ , 12.5, 12.8.  $\text{C}_4\text{H}_6\text{ON}_4 \cdot \text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$ , 12.5%. Found in dried material: N, 45.1, 43.6; C, 37.9; H, 4.9.  $\text{C}_4\text{H}_6\text{ON}_4$  requires N, 44.4; C, 38.1; H, 4.8%). The hydrazide is moderately easily soluble in alcohol but insoluble in benzene, chloroform, and ether. It reduces ammoniacal silver nitrate slowly, but not Fehling's solution.

The *picrate* crystallises from water (1 in 85 parts of boiling water) in anhydrous yellow needles, m. p.  $223^{\circ}$  (decomp.) (Found in air-dried salt by nitron estimation: picric acid, 64.8.



requires picric acid, 64.5%).

*Glyoxaline-4(5)-carboxyazide* (III).—A mixture of the hydrazide (6.3 g.), concentrated hydrochloric acid (7.0 c.c.), and a little ice was treated at  $0^{\circ}$  with sodium nitrite (7.0 g. in 15 c.c. of water). After 15 minutes, the *azide* was collected and washed with ice-water, 8.0 g. of slightly moist material, decomp.  $137^{\circ}$  (explosively), being obtained [Found in material dried at  $100^{\circ}$ : N (Dumas), 51.1.  $\text{C}_4\text{H}_3\text{ON}_5$  requires N, 51.0%]. It crystallised from 95% alcohol in minute stout rods.

When the azide is heated with water on the water-bath, gas is evolved and a dark green solution is produced, from which a *picrate* can be obtained; this chars at  $230^{\circ}$  after previous darkening (Found in dried material: picric acid, 66.4.  $\text{C}_7\text{H}_8\text{ON}_6 \cdot 2\text{C}_6\text{H}_3\text{O}_7\text{N}_3$  requires picric acid, 69.4%). Attempts to regenerate the base from the *picrate* were unsuccessful.

*4(5)-Carbethoxyaminoglyoxaline* (IV).—The azide (6.3 g.) was heated under reflux with absolute ethyl alcohol (50 c.c.) for 4 hours, the solvent removed, the residue dissolved in a little dilute hydrochloric acid and treated with charcoal, and the filtered solution concentrated to a few c.c. and basified with anhydrous sodium carbonate; the *carbethoxyamino*-derivative (3.0 g.; yield, 42.2%) obtained crystallised from boiling water, in which it was readily soluble, in anhydrous, colourless, hexagonal plates, m. p.  $180^{\circ}$  (Found in dried material: N, 27.2.  $\text{C}_6\text{H}_5\text{O}_2\text{N}_3$  requires N, 27.1%). It is very soluble in alcohol, moderately easily soluble in benzene, sparingly in chloroform, but insoluble in ether. With Pauly's reagent it gives a deep red solution. The hydrochloride regenerated from the *picrate* was obtained as a gum, which did not crystallise.

The *picrate* crystallises from boiling water (1 in 60 parts) in anhydrous, golden, hexagonal, prismatic needles, decomp.  $210^{\circ}$

(sintering from  $203^{\circ}$ ) (Found in substance dried at  $100^{\circ}$ : picric acid, 59.6, 59.8.  $C_6H_5O_2N_3, C_6H_3O_7N_3$  requires picric acid, 59.6%).

The *nitrate* crystallises from water, in which it is moderately easily soluble, in anhydrous, colourless, hexagonal prisms, decomp.  $143^{\circ}$  (Found in salt dried at  $100^{\circ}$ : nitric acid, by nitron method, 29.1.  $C_6H_5O_2N_3, HNO_3$  requires nitric acid, 28.9%).

4(5)-*Carbomethoxyaminoglyoxaline*, similarly prepared from the azide and methyl alcohol (yield, about 50%), crystallises from water (1 in 8 parts, boiling) in anhydrous diamond-shaped plates, m. p.  $175^{\circ}$  (Found in material dried at  $100^{\circ}$ : N, 30.3.  $C_5H_7O_2N_3$  requires N, 29.8%). It is very soluble in alcohol, sparingly soluble in ether, and insoluble in benzene and chloroform. With Pauly's reagent, a rich port-wine colour is produced. The *picrate* crystallises from water, in which it is sparingly soluble, in anhydrous irregular prisms, which blacken at about  $240^{\circ}$  and decompose at  $243^{\circ}$  (Found: picric acid, 61.4, 61.6.  $C_5H_7O_2N_3, C_6H_3O_7N_3$  requires picric acid, 61.9%).

5(4)-*Nitro-4(5)-carbomethoxyaminoglyoxaline* (V).—The preceding nitrate (1 g.) was added to concentrated sulphuric acid (2 c.c.) at  $0^{\circ}$  during 10 minutes and then warmed on the water-bath until effervescence began (10 minutes). The *nitro*-derivative, which separated (yield, 58%) when the mixture was poured on ice, crystallised from water in large, anhydrous, rhomboidal plates, m. p.  $234^{\circ}$  (decomp.) (Found in material dried at  $100^{\circ}$ : N, 28.3.  $C_6H_5O_4N_4$  requires N, 28.0%). It is soluble to the extent of 1 in 400 parts of boiling water and also in hot alcohol, but insoluble in benzene, chloroform, and ether. No colour reaction is given with Pauly's reagent.

4-*Nitro-5-amino-1-methylglyoxaline* (VII).—5-Chloro-4-nitro-1-methylglyoxaline (6.6 g.) and alcoholic ammonia (3.5%; 90 c.c.) were heated together at  $140^{\circ}$  for 4 hours. The *nitro*-compound, which had separated (3.7 g.; yield, 63.7%), crystallised from water (solubility, 1 part in 170 parts, boiling) in yellow, anhydrous, rectangular plates, m. p.  $303^{\circ}$  (decomp.) (Found in material dried at  $100^{\circ}$ : C, 33.7; H, 4.3; N, 39.8.  $C_4H_6O_2N_4$  requires C, 33.8; H, 4.2; N, 39.4%). It is soluble in concentrated hydrochloric acid, but not in dilute acid, alcohol, chloroform, or ether. It dissolves in boiling glacial acetic acid, forming apparently an acetate, for when the diluted solution is treated successively with sodium nitrite and alkaline  $\beta$ -naphthol a greenish-blue colour is obtained. The *nitro*-compound does not give a *picrate* when treated with aqueous picric acid.

*Action of cold 16% hydrochloric acid.* When the *nitro*-compound (2.6 g.) was added to 16% hydrochloric acid (10.4 c.c.) and stirred,

the solution darkened considerably and after some minutes much heat was evolved, the temperature rose from  $21^{\circ}$  to  $47^{\circ}$ , effervescence ensued, nitrous acid was liberated, and crystals immediately separated (1.1 g.), leaving a mother-liquor (M). The solid did not give a Pauly reaction, or a coloured solution with sodium  $\beta$ -naphthoxide after treatment with nitrous acid. When it was recrystallised from a little water (10 c.c.; charcoal), a small crop (0.1 g.), m. p.  $140^{\circ}$ , was obtained; the mother-liquor on concentration gave only a dark brown gum. The mother-liquor (M) on concentration gave 0.3 g., m. p.  $140^{\circ}$ . The combined mother-liquors were mixed with an excess of aqueous sodium hydroxide, and the volatile amines distilled into hydrochloric acid. After evaporation, the residue gave 0.5 g. insoluble in absolute alcohol (Found: Cl, 64.8. Calc. for  $\text{NH}_4\text{Cl}$ : Cl, 66.4%) and 0.6 g., m. p.  $195\text{--}200^{\circ}$ , soluble in absolute alcohol (Found: Cl, 53.5. Calc. for  $\text{NH}_2\text{Me}, \text{HCl}$ : Cl, 52.6%). The alkaline solution yielded, after acidification and treatment with calcium chloride in ammoniacal solution, 0.4 g. containing 97% of calcium oxalate.

$\alpha$ -Methylamino- $\alpha$ -hydroxyacetamide (IX) is moderately easily soluble in hot water, but much less so in cold, and crystallises in long, anhydrous, pale brown needles, m. p.  $140^{\circ}$ . Its aqueous solution is neutral to litmus (Found in material dried at  $100^{\circ}$ : C, 34.0; H, 7.8; N, 26.7, 27.0.  $\text{C}_3\text{H}_8\text{O}_2\text{N}_2$  requires C, 34.6; H, 7.7; N, 26.9%).

The author is indebted to Mr. R. H. Klein, F.I.C., for making some of the analyses recorded in this paper.

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## XLI.—*Internal Equilibrium in Sulphur. Part II. Amorphous Sulphur ( $\text{S}_\mu$ ) as a Gel, and the Tyndall Effect in Liquid Sulphur.*

By DALZIEL LLEWELLYN HAMMICK and MICHAEL ZVEGINTZOV.

It has long been recognised (Krøyt, *Z. physikal. Chem.*, 1909, 65, 486; Hammick and Holt, J., 1926, 1995) that as molten sulphur is heated, it becomes richer in one or more forms which are less miscible with other liquids and give rise to the peculiar properties of liquid sulphur. It also appears to have been generally assumed, with Smith and his co-workers, that the insoluble, amorphous solid obtained when molten sulphur is chilled, allowed to harden, and

then extracted with carbon disulphide, is identical with one of the constituents present in the melt. As is well known, the familiar allotropic line (Smith and Carson, *Z. physikal. Chem.*, 1907, 57, 685) giving the percentages of  $S_\mu$  present in liquid sulphur at various temperatures is constructed from data derived from estimates of the amount of insoluble sulphur present in specimens of sulphur chilled from these temperatures.

In the course of our experiments on equilibria in the system sulphur-sulphur chloride (J., 1928, 1785), we noticed that in the presence of even quite small proportions of its chloride the element could be heated to 160–180° without any great increase in viscosity. For instance, mixtures of pure sulphur (98%) with sulphur chloride (2%) heated in sealed tubes for various periods ( $\frac{1}{2}$ –2 hours) at 140° and 180° gave quite mobile, dark-coloured liquids. Most of these mixtures on sudden chilling solidified almost completely, and it was found that a considerable proportion of the solid separating was insoluble in carbon disulphide, *i.e.*, the solid contained  $S_\mu$ . In many of the tubes, however, solidification did not occur on chilling, and in some cases it was possible to open them and treat the contents with carbon disulphide while the latter were still metastable and fluid. The supercooled mixture was completely miscible with this solvent. It would thus appear that  $S_\mu$ , insoluble in carbon disulphide, does not exist in the fluid sulphur-sulphur chloride mixtures that have been chilled from high temperatures, but makes its appearance when such mixtures deposit solid. Only when the concentration of sulphur chloride was not more than 2% was it possible to demonstrate this distinction between two specimens of sulphur which had been treated in exactly the same way in respect to heating and chilling, but differed by the circumstance that in one case the separation of solid had been avoided and with it the production of  $S_\mu$ . Nevertheless, the fact that the mere heating of sulphur and chilling does not by itself yield sulphur insoluble in carbon disulphide (or  $S_\mu$ ) was confirmed in numerous cases where solutions of sulphur in sulphur chloride and in other solvents, such as xylene, pyridine, and quinoline, were chilled from temperatures between 150° and 180° without solid separating and found to be completely miscible with carbon disulphide.

In the light of the above observations it becomes necessary to account for the insolubility in carbon disulphide of chilled sulphur by a hypothesis that does not postulate the pre-existence of the insoluble  $S_\mu$  in the liquid from which it is produced on chilling, and we have therefore come to the conclusion that insoluble amorphous sulphur is probably a gel. The plasticity of freshly chilled sulphur obviously accords with this supposition; the "setting" of plastic

sulphur to the hard amorphous  $S_{\mu}$  is, we suggest, analogous to the hardening of gels such as those of hydrated oxides (silica gels, etc.). In further support of our view we adduce the following observations.

(i) *The solubility of  $S_{\mu}$  in various solvents.* "Chilled" sulphur, prepared by distilling pure sulphur into cold water, was found to be insoluble in cold carbon disulphide, sulphur chloride, pyridine, quinoline, and xylene, whether it was in the rubber-like, plastic condition or had been kept until it had set to a hard mass. Rapid solution occurred, however, in the above solvents at temperatures above (roughly)  $120^{\circ}$ . For instance, 50% by weight of amorphous sulphur added to boiling sulphur chloride ( $138^{\circ}$ ) liquefied and dissolved completely in 5 seconds. A similar result was observed in quinoline at  $130^{\circ}$ ; 10% of amorphous sulphur also dissolved readily and rapidly in liquid benzoic acid at  $123^{\circ}$ . In pyridine (b. p.  $115^{\circ}$ ), dissolution was much slower and the amorphous sulphur did not liquefy completely: 10 g. dissolved completely, however, in 100 g. of solvent in 1 minute.

That amorphous sulphur (or  $S_{\mu}$ ) dissolves in hot solvents has, of course, long been known; but the fact that it does so has been ascribed to the effect of temperature in promoting its rapid change into soluble  $S_{\lambda}$ . It does not seem to be generally realised, however, that even at  $140^{\circ}$  it takes about 3 hours for "internal equilibrium" to be set up in liquid sulphur, and that "amorphous sulphur" kept at the natural f. p. of sulphur ( $114.5^{\circ}$ ) for 10 hours still contains 50% of insoluble sulphur (Smith and Carson, *loc. cit.*). Further, the authors (*loc. cit.*) found that in sulphur chloride solution at  $148^{\circ}$ ,  $1\frac{1}{2}$  hours were required to establish equilibrium. On the other hand, if  $S_{\mu}$  is really a gel, it might be expected, like other gels such as rubber, gelatin, resins, etc., to show a more or less abrupt change in properties at and above the temperatures at which the gel structure is destroyed. It is significant that rapid dissolution of  $S_{\mu}$  in solvents begins at about  $120^{\circ}$ , i.e., at about the melting point of crystalline sulphur, which may possibly be the continuous phase in the gel.

(ii) *The Tyndall effect in liquid sulphur.* The hypothesis that chilled sulphur or  $S_{\mu}$  is a gel led to the expectation that the liquid from which it is produced might show the properties of a sol. Liquid sulphur was therefore examined for the Tyndall effect. It is well known that the production of liquids in a state of optical purity is a matter of considerable difficulty. The sulphur used was therefore carefully purified by crystallisation from pure carbon disulphide and then by distillation, first under ordinary pressure and finally in a vacuum. It was then introduced into the side bulb of an apparatus of Pyrex glass, consisting of a cylindrical observation

tube with flat top and bottom, the apparatus was exhausted with a mercury pump and sealed, and the sulphur distilled into the observation tube, remelted, and tipped back into the distillation bulb.\* This was done six times, in order to wash out the observation tube, which was then surrounded by a small electric resistance furnace. A beam of light from a 500-watt lamp was focused through a window in the side of the furnace into the melted sulphur, which was observed through the top. A well-defined Tyndall beam of polarised scattered light was observed at all temperatures from the melting point up to  $200^{\circ}$ , at which the deep colour of the liquid sulphur prevented further observations.

Having obtained this characteristic indication of the presence of colloidal particles in liquid sulphur, we attempted to measure the intensity of the scattered light over a range of temperature in order to find out whether there was any correlation between the concentration of colloidal particles and the increase of viscosity of liquid sulphur that occurs at about  $160^{\circ}$ . The exciting beam was caused to enter the observation vessel as near to the bottom as possible, and at the same time light from a small electric-light bulb (3-watt) was passed vertically up through the base. By varying the resistance in circuit with the small bulb, it was possible roughly to match, by observation through the top of the tube, the intensity of the light transmitted from the control lamp through the liquid sulphur with the intensity of the Tyndall light. Both the direct and the scattered light had to traverse very nearly the same depth of liquid (about 8 cm.). The current flowing through the "control" lamp was measured on a milliammeter, and the temperature of the sulphur was varied by altering the resistance in series with the electric heating furnace that surrounded the observation tube. No great precision can be claimed for the observations made; nevertheless, the rather surprising conclusion can be drawn from them that, as far as could be detected by the rough apparatus used, no appreciable alteration in the intensity of the scattered Tyndall light could be observed between  $125^{\circ}$  and  $200^{\circ}$ . A typical series of measurements was :

Temp. of furnace ...	$128^{\circ}$	$135^{\circ}$	$153^{\circ}$	$165^{\circ}$	$180^{\circ}$	$200^{\circ}$
Current in control lamp (amp.) ...	0.45	0.43	0.435	0.45	0.44	0.45

Before these experiments could be repeated with more refined apparatus, however, a private communication from W. L. Cousins

\* In order to test this method for obtaining liquids optically "pure," experiments were carried out in similar pieces of apparatus with carbon tetrachloride and phenol. In each case two washings of the observation tube with distillate were sufficient to give liquids in which no Tyndall effect could be observed.



and B. Lange in Berlin informed us of results, to be published shortly, which they had obtained in measuring the intensity of polarisation of the Tyndall light in molten sulphur, and further work on the matter was abandoned.

In conclusion, it may be noted that the view that insoluble sulphur ( $S_\mu$ ) is a gel removes the difficulty in accounting for the fact that, although it is metastable with respect to crystalline sulphur, the latter is vastly more soluble.

### *Summary.*

Experiments are described showing that insoluble sulphur (amorphous sulphur or  $S_\mu$ ) is not present as such in liquid sulphur but makes its appearance when the liquid solidifies. It is therefore suggested that  $S_\mu$  is in reality a gel, and in support of this hypothesis its ready solubility in certain solvents at temperatures above the m. p. of crystalline sulphur (possible continuous phase) is noted, and the presence of colloidal particles in pure molten sulphur is established by observations on the Tyndall effect.

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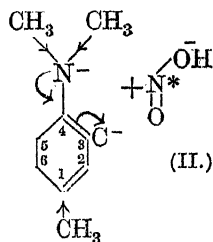
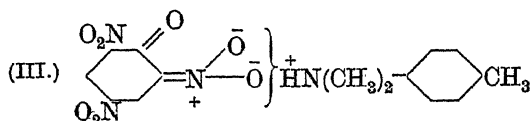
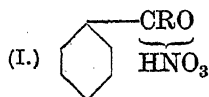
## XLII.—*Nitrous Acid as a Nitrating Agent. Part I.* *The Nitration of Dimethyl-p-toluidine.*

By HERBERT HENRY HODGSON and ARNOLD KERSHAW.

NITROUS acid *nitrates* dimethyl-*p*-toluidine, giving at least 80% of 3-nitrodimethyl-*p*-toluidine (3-nitro-4-dimethylaminotoluene): nitric acid at the same dilution is practically inactive. *o*-Nitrosation analogous to the *p*-nitrosation of dimethylaniline does not appear to take place. Since 2-nitrodimethyl-*p*-toluidine is produced by the normal nitration process, the mechanism of the above reaction must differ from that of ordinary nitration.

Lapworth and Robinson (*Mem. Manchester Phil. Soc.*, 1928, **72**, 47) explain the apparently anomalous ortho-nitration of benzaldehyde and of acetophenone by assuming the formation of an additive complex (I) of nitric acid and the unsaturated group, which then favours nitration in the ortho-position. In the light of this conception it may be assumed that the nitrogen atom and the 3-carbon atom of dimethyl-*p*-toluidine, both strongly activated (II), produce a negative field which attracts the polarised nitrous acid,  $\text{H}\ddot{\text{O}}\text{N}^+\text{O}^-$ , and, by rendering its nitrogen\* less positive, makes it prone to oxidation: the free nitrous acid in the solution oxidises the nitrous

acid component of the complex (II) to nitric acid, with evolution of nitric acid and nitrous oxides and subsequent nitration at the activated 3-carbon atom.



The m. p.'s of the picrates of the two pairs of nitro-compounds studied show definitely that the lower m. p. is associated with the greater chelation (in the case of the 3-nitro-compounds) and conversely that the higher m. p. accompanies increased salt-formation (with the 2-nitro-compounds).

The brilliant red unstable compound formed when dimethyl-*p*-toluidine is mixed with picric acid may perhaps be due to temporary formation of the salt of the *aci*-form of picric acid (III), since such salts have a bright red colour.

#### EXPERIMENTAL.

*Preparation of Dimethyl-p-toluidine.*—A mixture of *p*-toluidine (72.7 g.), methyl iodide (96.5 g.), and water (100 c.c.) was heated under reflux (2–3 hours), and then exactly neutralised with aqueous sodium hydroxide. A further addition of methyl iodide (96.5 g.) was made, and after being again heated until the odour of the methyl iodide had vanished, the mixture was rendered faintly alkaline and steam-distilled. The oily layer of the distillate was treated with acetic anhydride (2–3 c.c. at a time) until no rise of temperature subsequently occurred, a further 5 c.c. were added (total addition, about 35 c.c.) and the mixture was heated on the water-bath for 1 hour, poured into water (200 c.c.), shaken well to decompose the acetic anhydride, neutralised with sodium hydroxide, and steam-distilled; pure dimethyl-*p*-toluidine (33 g.) passed over (b. p. 207°) (Found: N, 10.6. Calc.: N, 10.4%).

The *picrate*, prepared from equimolecular quantities of the base and picric acid in hot alcohol, separated on cooling in elongated prisms, m. p. 128° after recrystallisation from alcohol (Found: N, 15.2. C<sub>15</sub>H<sub>16</sub>O<sub>7</sub>N<sub>4</sub> requires N, 15.4%). When dimethyl-*p*-toluidine is mixed with solid picric acid, a very deep red compound is produced which soon changes into a bright yellow one. Cold alcoholic solutions when mixed give a red solution, from which the yellow *picrate* crystallises, although its alcoholic solution is yellow.

*Action of Nitrous Acid on Dimethyl-p-toluidine.*—The base (10 g.), dissolved in a mixture of concentrated hydrochloric acid (28 c.c.) and water (20 c.c.), was gradually treated at 0° with sodium nitrite (16 g. in 100 c.c. of water). Reaction began on addition of the first drop, the solution became red, and nitric oxide containing a detectable quantity of nitrous oxide was evolved; when about half the sodium nitrite had been added, the deep red solution became turbid owing to separation of the oily reaction product. After 1 hour, the mixture was treated with urea to remove any excess of nitrous acid, neutralised with sodium hydroxide, and steam-distilled, and the distillate (1200 c.c.) was extracted with ether. The extract, after being shaken three times with dilute hydrochloric acid (40 c.c.; 1 part of conc. acid and 2 parts of water), was evaporated and nitrosomonomethyl-p-toluidine (1.6 g.) was obtained from the residue by steam-distillation. The nitrosoamine gave a brilliant colour in the Liebermann reaction and crystallised from light petroleum in almost colourless prisms, m. p. 49.5° (Bamberger and Wulz, *Ber.*, 1891, **24**, 2081, give m. p. 52—53°) (Found: N, 18.8. Calc.: N, 18.7%).

The aqueous acid extract (above) was made faintly alkaline and steam-distilled; 3-nitrodimethyl-p-toluidine (10.5 g.) passed over as a red oil, which, after solidifying, crystallised from aqueous alcohol in red needles, m. p. 26° (Found: N, 15.3.  $C_9H_{12}O_2N_2$  requires N, 15.5%). The *picrate*, prepared as described above, crystallised from alcohol in bright yellow, elongated, rectangular plates, m. p. 129° to a red liquid after softening (Found: N, 17.0.  $C_{15}H_{15}O_9N_5$  requires N, 17.1%). The amine and its *picrate* were identified by comparison with the synthetic compounds (below).

Nitric acid of the same concentration as the nitrous acid employed above was practically inactive, showing that the above nitration could not have been due to nitric acid present in the nitrous acid as initially generated.

*Synthesis of 3-Nitrodimethyl-p-toluidine.*—4-Chloro-3-nitrotoluene (6 g., prepared from 3-nitro-p-toluidine) was heated under reflux with a solution of dimethylamine (in slight excess of the theoretical quantity) in alcohol (40 c.c.) for 20 hours. The alcohol was then removed by distillation, and the reaction product steam-distilled; 3-nitrodimethyl-p-toluidine, obtained in theoretical yield, crystallised from dilute alcohol in red needles, m. p. 26° (Found: N, 15.4%). The *picrate* melted at 129° (Found: N, 17.3%).

*Nitration of Dimethyl-p-toluidine.*—The amine (3 g.) in concentrated sulphuric acid (7 c.c.) was gradually treated at 0° with a mixture of nitric acid (1.4 c.c.; *d* 1.5) and sulphuric acid (2 c.c.). After 12 hours, the whole was poured on ice (200 g.), neutralised;

and submitted to steam-distillation; 2-nitrodimethyl-p-toluidine, which distilled in almost theoretical yield, crystallised from glacial acetic acid, on dilution with water, in large vermilion plates, m. p. 37° (Found: N, 15.4.  $C_9H_{12}O_2N_2$  requires N, 15.5%). The *picrate* crystallised from alcohol in elongated yellow prisms, m. p. 141—143° (Found: N, 17.2.  $C_{15}H_{15}O_9N_5$  requires N, 17.1%).

*o*-Nitrodimethylaniline was readily prepared in theoretical yield by heating an alcoholic solution (140 c.c.) of *o*-chloronitrobenzene (15g.) and dimethylamine (in slight excess of the theoretical quantity) under reflux for 6 hours (compare Weissenberger, *Monatsh.*, 1912, **33**, 821). The *picrate* crystallised from alcohol in greenish-yellow needles, m. p. 103° (Found: N, 18.0.  $C_{14}H_{13}O_9N_5$  requires N, 17.7%).

*Dimethylaniline picrate* crystallises from alcohol in greenish-yellow plates, m. p. 159° (Found: N, 16.2.  $C_{14}H_{14}O_7N_4$  requires N, 16.0%).

3-Nitrodimethylaniline *picrate* separates from alcohol in elongated yellow plates, m. p. 119° (Found: N, 17.4.  $C_{14}H_{13}O_9N_5$  requires N, 17.7%).

All the above nitro-bases give yellow solutions in non-dissociating solvents, whereas in dissociating media, and in particular in phenol, intense red solutions are formed.

The authors desire to thank Messrs. J. W. Leitch & Co. for gifts of some of the chemicals used in this investigation.

TECHNICAL COLLEGE, HUDDERSFIELD. [Received, November 30th, 1929.]

### XLIII.—*The Variation of Phenol Coefficients in Homologous Series of Phenols.*

By CHARLES EDWARD COULTHARD, JOSEPH MARSHALL,  
and FRANK LEE PYMAN.

THE introduction into medicine of the antiseptic, hexylresorcinol, was the outcome of work by Johnson and Lane (*J. Amer. Chem. Soc.*, 1921, **43**, 348) and Dohme, Cox, and Miller (*ibid.* 1926, **48**, 1688) in which the influence of alkyl substituents upon the germicidal value of resorcinol was studied. It was shown that the germicidal value of 4-*n*-alkylresorcinols rose to a maximum at 4-*n*-hexylresorcinol, which had a phenol coefficient of 50, the values for *n*-amyl- and *n*-heptyl-resorcinol being 33 and 30 respectively. It was further shown that the antiseptic values of the *n*-alkyl-resorcinols were greater than those of branched-chain alkylresorcinols having the same number of carbon atoms.

Exact information as to the effect of alkyl substituents upon the antiseptic value of phenol and its homologues is somewhat scanty and therefore it appeared to be of interest to make a systematic study of the variation of the phenol coefficients in the homologous series of *n*-alkylphenols, *n*-alkylcresols, and *n*-alkylguaiacols.


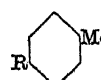


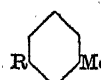
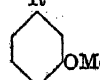
For the determination of phenol coefficients, the Rideal-Walker technique was closely followed, but owing to the sparing solubility of most of the compounds in water, solutions in dilute aqueous sodium hydroxide were employed, care being taken to keep the concentration of sodium hydroxide below lethal strength. In most cases, initial solutions of 0.1% of the compound in *N*/100-sodium hydroxide were used. The results are in Table I.

Comparing the vertical columns in this table, it will be seen that the phenol coefficients of the *p*-*n*-alkylphenols are, in general, considerably less than those of the corresponding *n*-alkylcresols, and the values of the *n*-alkylguaiacols are comparatively trivial. In comparing the horizontal columns, it will be noticed that the antiseptic value of the compounds increases generally with the number of carbon atoms in the side chain up to the *n*-amyl derivative and then diminishes.

Of the *n*-amylcresols, 4-*n*-amyl-*m*-cresol has been studied in some detail, and has been found to have high phenol coefficients (200 to 300), not only when tested against *Bacillus typhosus* (which is employed in the Rideal-Walker method), but also against various strains of *Streptococcus* and *Staphylococcus*. Since, in addition, its toxicity is comparatively low, it may prove to be of value in medicine.

TABLE I.

## Phenol coefficients.

	<i>p</i> - <i>n</i> -Alkyl-phenols.	4- <i>n</i> -Alkyl- <i>m</i> -cresols.	3- <i>n</i> -Alkyl- <i>p</i> -cresols.	5- <i>n</i> -Alkyl- <i>o</i> -cresols.	3- <i>n</i> -Alkyl- <i>o</i> -cresols.	4- <i>n</i> -Alkyl-guaiacols.
	R	R	Me	R	R	R
						
R.	OH	OH	OH	OH	OH	OH
CH <sub>3</sub>	2.5	—	—	—	—	2.7
C <sub>2</sub> H <sub>5</sub>	7.5	12.5†	12.5	15	—	2
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	20	34	—	—	—	5
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	70*	100	95	110	60	25
<i>n</i> -C <sub>5</sub> H <sub>11</sub>	104	280	250	300	250	25
<i>n</i> -C <sub>6</sub> H <sub>13</sub>	90	275	175	100	180	9
<i>n</i> -C <sub>7</sub> H <sub>15</sub>	20	30	—	—	—	—

\* The phenol coefficient of *o*-*n*-butylphenol was 75.

† The phenol coefficient of 6-ethyl-*m*-cresol (Me : OH : Et = 1 : 3 : 6) was 15.

*Preparation of n-Alkylphenols, n-Alkylcresols, and n-Alkylguaiacols.*

All the alkyl derivatives were prepared by reduction of the corresponding ketones by Clemmensen's method. The ketones were prepared by four methods: (1) the Nencki condensation of acid and phenol using zinc chloride, (2) the Fries isomerisation of phenyl esters by means of aluminium chloride, (3) the isomerisation of phenyl esters by zinc chloride, and (4) condensation of acids with phenols by means of phosphorus oxychloride.

(1) The Nencki reaction is well known to give good yields of 4-acylresorcinols or 2-acylquinols when resorcinol or quinol is condensed with fatty acids and zinc chloride. Goldzweig and Kaiser (*J. pr. Chem.*, 1891, **43**, 86) state that pyrocatechol does not react when employed in the Nencki reaction and it would appear that this statement has been accepted, although Neitzel (*Ber.*, 1891, **24**, 2863) mentions that acetylpyrocatechol is "apparently" produced by this method. He did not, however, obtain it in a pure state owing to the similarity in solubility of pyrocatechol and acetylpyrocatechol. We are able to confirm the formation of acetylpyrocatechol and other acylpyrocatechols by the Nencki method, and have separated them from unchanged pyrocatechol in each case by distillation under diminished pressure.

Attempts to apply the Nencki reaction to monoalkyl ethers of dihydroxybenzenes have given poor yields, but positive results were obtained in the formation of pæonol from resorcinol monomethyl ether and acetic acid, and in the preparation of acetovanillone and its homologues from guaiacol and fatty acids. Attempts to condense quinol monomethyl ether with acetic acid, however, gave a negative result. The Nencki reaction has been little used for the condensation of monohydric phenols with fatty acids, but Michael and Palmer (*Amer. Chem. J.*, 1885, **7**, 275) obtained *p*-acetylphenol in this manner, and Goldzweig and Kaiser (*loc. cit.*) obtained *p*-propionylphenol similarly, although the yield is not stated in either case. We have condensed a series of fatty acids with phenol by this method and have obtained the *p*-acylphenols in poor yield, *viz.*, 2–10% of the theoretical, and have observed that small quantities of the *o*-acylphenols are formed simultaneously. The sole products obtained from *m*-cresol in the Nencki reaction were the 4-acyl-*m*-cresols, as would be expected from the well-known fact that an alkyl group in the meta-position to the hydroxyl induces substitution in the neighbourhood of the hydroxyl (Auwers and Mauss, *Annalen*, 1928, **464**, 293), but here again the yields are poor.

(2) A considerable number of acylphenols and acylcresols have been made by the Fries isomerisation under the conditions described

by Rosenmund and Schnurr (*Annalen*, 1928, 460, 56), viz., heating the appropriate ester with 1.1 molecules of aluminium chloride. Attempts to prepare acylguaiacols similarly were unsuccessful, but the publication of a paper by Pfeiffer and Haack (*Annalen*, 1927, 460, 156) on the combination of aluminium bromide with ethers in molecular proportion led us to suspect that a similar combination occurred between aluminium chloride and guaiacol esters, and that this prevented the aluminium chloride from producing isomerisation. In later experiments, two molecular proportions of aluminium chloride were consequently added to guaiacol esters and 4-acyl-guaiacols were then produced together with a proportion of the corresponding acylpyrocatechols. The position taken up by the acyl group was proved by the facts (1) that guaiacyl acetate gave acetovanillone, (2) that guaiacyl butyrate gave a ketone which was reduced to a butylguaiacol identical with that obtained by Nomura and Hotta (*Sci. Rep. Tōhoku Imp. Univ.*, 1925, 14, 119) by the reduction of zingerone, and (3) that the propylguaiacol obtained in the same manner from guaiacyl propionate was identical with dihydroeugenol.

(3) Pope (Brit. Pat. 287,967) has described a method for the preparation of 4-*n*-alkylresorcinols by isomerisation of resorcinol monoacyl esters by heating with zinc chloride. We have found that, although this method gives good yields (80—90%) of resacetophenone<sup>1</sup> and 4-*n*-hexoylresorcinol when applied to resorcinol monoacetate and mono-*n*-hexoate, it gives only poor yields of acylphenols when applied to esters of phenol, *m*-cresol, and guaiacol.

(4) The condensation of guaiacol and acetic acid by means of phosphorus oxychloride gave isoacetovanillone (5-acetylguaiacol), which was obtained previously by Schneider and Kraft (*Ber.*, 1922, 55, 1892) by condensing guaiacol and acetic anhydride by means of sulphuric acid. Propionic and butyric acids were also condensed with guaiacol by means of phosphorus oxychloride, and gave compounds isomeric with 4-propionylguaiacol and 4-*n*-butyrylguaiacol, which are doubtless 5-*propionylguaiacol* and 5-*n-butyrylguaiacol*.

#### EXPERIMENTAL.

(1) *The Nencki Reaction.*—*o*- and *p*-Acetylphenols. Phenol (150 g.) was added to a hot solution of anhydrous zinc chloride (200 g.) in glacial acetic acid (100 c.c.) and the mixture was boiled for 1 hour. After the mass had cooled, water was added and the product was distilled with steam. The oil separated from the distillate was dissolved in excess of warm 5*N*-sodium hydroxide, and from this solution, on cooling, pale yellow crystals were deposited which after decomposition with dilute hydrochloric acid gave

*o*-acetylphenol (5 g.; yield, 2%\*) having b. p. 110°/15 mm. and m. p. 28° (Found: C, 70.5; H, 5.8. Calc.: C, 70.6; H, 5.9%). The oxime melted at 112°. Auwers (*Ber.*, 1925, 58, 36) gives b. p. 218° and m. p. of oxime 112°. The non-volatile oil remaining after the steam distillation was distilled under diminished pressure and gave *p*-acetylphenol (7 g.; yield, 3%) having b. p. 190°/15 mm. and m. p. 106—107°. Michael and Palmer (*loc. cit.*) give m. p. 108° and Perkin (*J.*, 1897, 71, 805) gives m. p. 107°.

The great difference in boiling point exemplified in the case of the *o*- and *p*-acetylphenols is found generally for *o*- and *p*-acylphenols and their methyl homologues. The *o*-hydroxyketones differ further from *p*-hydroxyketones in being volatile in steam and in giving red to violet colorations with ferric chloride. Moreover, the sodium salts of the *o*-acylphenols are readily obtained in yellow crystals freely soluble in water, and are easily precipitated by a small excess of alkali, whereas the sodium salts of the *p*-compounds are colourless and are easily soluble in water and in dilute sodium hydroxide solution.

As a general rule, the phenylhydrazones of the *o*-compounds are more readily made than the *p*-compounds, as is known to be the case with the oximes.

*p*-Propionylphenol was prepared by the method of Goldzweig and Kaiser (*loc. cit.*) in 10% yield.

*p*-*n*-Valerylphenol was obtained in 5% yield accompanied by the *o*-compound, of which the presence was indicated through the production of a violet colour on the addition of ferric chloride to an alcoholic solution of the steam-distillate of the reaction product. *p*-*n*-Valerylphenol has b. p. 210°/15 mm. and crystallises from benzene—light petroleum in cubes, m. p. 62—63° (Found: C, 74.0; H, 7.9.  $C_{11}H_{14}O_2$  requires C, 74.2; H, 7.8%).

*p*-*n*-Hexoylphenol (yield, 8%) forms colourless plates, m. p. 63—64°, from benzene (Found: C, 75.1; H, 8.4.  $C_{12}H_{16}O_2$  requires C, 75.0; H, 8.3%).

*p*-*n*-Heptoylphenol (yield, 9%; b. p. 220°/15 mm.) crystallises from benzene in well-formed prisms, m. p. 93—94° (Found: C, 75.9; H, 8.6.  $C_{13}H_{18}O_2$  requires C, 75.7; H, 8.7%).

*p*-Heptoylphenyl benzoate crystallises from alcohol in needles, m. p. 92—93° (Found: C, 77.0; H, 7.1.  $C_{20}H_{22}O_3$  requires C, 77.4; H, 7.1%).

4-Propionyl-*m*-cresol was isolated from the product of the fusion of propionic acid and *m*-cresol with zinc chloride by distillation with steam and rectification of the oil obtained in a vacuum. The

\* Yields are given in % of the theoretical, and the substances are colourless except where it is otherwise stated.



fraction, b. p. 125—135°/15 mm., was crystallised from dilute alcohol, giving needles or plates, m. p. 45—46° (yield, 11%). It did not depress the melting point of 4-propionyl-*m*-cresol, prepared by the isomerisation of *m*-tolyl propionate, for which Auwers (*Annalen*, 1924, 439, 132) gives m. p. 45—46°.

4-*n*-Butyryl-*m*-cresol was similarly obtained from *m*-cresol and butyric acid (yield, 17%) and identified as the oxime, m. p. 74—75° (see page 288).

*Pæonol*. To zinc chloride (40 g.), dissolved in hot glacial acetic acid (40 c.c.), resorcinol monomethyl ether (25 g.) was added. The mixture was brought to the boiling point, allowed to cool in an oil-bath, and distilled with steam. The oil which distilled was separated by fractional distillation under diminished pressure into about 10 g. of unchanged resorcinol monomethyl ether and a fraction of higher boiling point from which 6 g. (29%) of *pæonol*, m. p. 50°, were obtained.

4-*Acetylpyrocatechol*. Pyrocatechol (25 g.), glacial acetic acid (50 g.), and zinc chloride (100 g.) were fused together in the usual manner. The mass was poured into water, and the solution extracted with ether. After distillation under diminished pressure, pyrocatechol and a fraction of b. p. about 180° (15 g.) were obtained. This was dissolved in hot benzene and allowed to cool; the crystals which separated were recrystallised and gave 8 g. (20%) of 4-acetylpyrocatechol, m. p. 116°. 4-*n*-Butyrylpyrocatechol and 4-*n*-hexoylpyrocatechol were obtained by exactly similar methods of procedure. Each was compared and found to be identical with the corresponding product obtained from the guaiacol ester by treatment with aluminium chloride.

*Acetovanillone*. To zinc chloride (100 g.) in hot glacial acetic acid (200 c.c.), guaiacol (100 g.) was added. The mixture was boiled gently under reflux for 3 hours, and acetic acid then distilled off under diminished pressure. After cooling, the residue was poured into water and extracted with ether. The extract was distilled under diminished pressure; a fraction, b. p. 170—190°, solidified and after recrystallisation from ether gave acetovanillone (5 g.; 4%), m. p. 113—114°.

4-*n*-Butyrylguaiacol and 4-*n*-hexoylguaiacol were prepared similarly and proved to be identical with the products, described later, obtained by the isomerisation of guaiacol esters with aluminium chloride; in each case considerable quantities of pyrocatechol and of the corresponding acylpyrocatechols were obtained as by-products.

(2) *The Fries Isomerisation*.—Phenyl butyrate, hexoate, and heptoate were converted into mixtures of *o*- and *p*-acylphenols by

heating with 1.1 mols. of aluminium chloride at 160—180° for 1—2 hours, and separated by distillation with steam or under diminished pressure.

*o-n-Butyrylphenol* (yield, 60%) had b. p. 124—126°/14 mm. and m. p. 8° (Found: C, 72.9; H, 7.3.  $C_{10}H_{12}O_2$  requires C, 73.2; H, 7.3%). Its *phenylhydrazone* is yellow and melts at 85—87° (Found: N, 11.0.  $C_{16}H_{18}ON_2$  requires N, 11.0%). *p-Butyrylphenol* (yield, 19%) has b. p. 200°/15 mm. and m. p. 91°. Perkin (J., 1889, 55, 546) gives m. p. 91°. *p-Butyrylphenyl benzoate* crystallises from alcohol in platelets, m. p. 106—107° (Found: C, 75.8; H, 6.0.  $C_{17}H_{16}O_3$  requires C, 76.1; H, 6.0%).

*o-n-Hexoylphenol* (yield, 50%) has b. p. 145—147°/15 mm. and crystallises from alcohol in prisms, m. p. 22° (Found: C, 74.8; H, 8.4.  $C_{12}H_{16}O_2$  requires C, 75.0; H, 8.3%). Its *phenylhydrazone* crystallises from alcohol in yellowish leaflets, m. p. 102—103° (Found: N, 9.6.  $C_{18}H_{22}ON_2$  requires N, 9.9%).

*o-n-Heptylphenol* (yield, 58%) has b. p. 172—174°/20 mm. and separates from alcohol in prisms, m. p. 24° (Found: C, 75.3; H, 8.7.  $C_{13}H_{18}O_2$  requires C, 75.7; H, 8.7%). Its *phenylhydrazone* separates from alcohol in yellow plates, m. p. 91—92°.

The isomerisation of *o*-tolyl acetate has been described by Auwers (Ber., 1925, 58, 36) and by Rosenmund and Schnurr (Annalen, 1927, 460, 56).

*5-Acetyl-o-tolyl benzoate* separates from dilute spirit in fine silky needles, m. p. 79—80° (Found: C, 75.5; H, 5.3.  $C_{16}H_{14}O_3$  requires C, 75.6; H, 5.5%).

*o*-Tolyl butyrate, valerate, and hexoate were isomerised by heating the ester with 1.1 mols. of aluminium chloride at 160—180° for  $\frac{1}{2}$  hour, and the *o*- and *p*-ketones were separated by distillation under diminished pressure.

*3-n-Butyryl-o-cresol* (yield, 60% at 160—180°; 40% at 100°) has b. p. 143°/11 mm. and solidifies in a freezing mixture (Found: C, 73.9; H, 7.9.  $C_{11}H_{14}O_2$  requires C, 74.2; H, 7.8%). Its oxime forms needles, m. p. 87—88°, from alcohol, and its *phenylhydrazone* separates from alcohol in yellow needles, m. p. 157—158° (Found: N, 10.3.  $C_{17}H_{20}ON_2$  requires N, 10.4%).

*5-n-Butyryl-o-cresol* (yield, 30% at the ordinary temperature in 2 days; 55% at 100°; and 30% at 160—180°), b. p. 195—200°/15 mm., forms prisms, m. p. 132—133°, from benzene (Found: C, 74.0; H, 7.8.  $C_{11}H_{14}O_2$  requires C, 74.2; H, 7.8%). The *phenylhydrazone* separates in yellowish plates, m. p. 110°.

*3-n-Valeryl-o-cresol* (yield, 46%) has b. p. 143—145°/15 mm. and m. p. 18° (Found: C, 74.6; H, 8.5.  $C_{12}H_{16}O_2$  requires C, 75.0; H, 8.3%). The *phenylhydrazone* forms pale yellow leaflets, m. p.

116—118°, from alcohol (Found : N, 9.8.  $C_{18}H_{22}ON_2$  requires N, 9.9%).

5-n-Valeryl-o-cresol (yield at 160°, 30%), b. p. 205°/15 mm., forms rhombic prisms, m. p. 103—104°, from benzene (Found : C, 74.8; H, 8.5.  $C_{12}H_{16}O_2$  requires C, 75.0; H, 8.3%). 5-n-Valeryl-o-tolyl benzoate separates from alcohol in small plates, m. p. 72—73° (Found : C, 77.0; H, 7.1.  $C_{19}H_{20}O_3$  requires C, 77.0; H, 6.7%). 5-n-Valeryl-o-cresol phenylhydrazone forms very pale yellow needles, m. p. 120—121° (Found : N, 9.8.  $C_{18}H_{22}ON_2$  requires N, 9.9%).

3-n-Hexoyl-o-cresol (yield, 60%), b. p. 152—154°/15 mm., separates from cold alcohol in prisms, m. p. 23° (Found : C, 75.9; H, 9.0.  $C_{13}H_{18}O_2$  requires C, 75.7; H, 8.7%). Its phenylhydrazone separates from alcohol in leaflets, m. p. 93—94° (Found : N, 9.3.  $C_{19}H_{24}ON_2$  requires N, 9.5%).

5-n-Hexoyl-o-cresol (yield at 160°, 25%), b. p. 200—205°/15 mm., separates from benzene in plates which fall to powder on drying at 50°; it then melts at 79—80° (Found : C, 75.7; H, 8.9.  $C_{13}H_{18}O_2$  requires C, 75.7; H, 8.7%). The benzoate crystallises from alcohol in shining leaflets, m. p. 59—60° (Found : C, 77.2; H, 6.9.  $C_{20}H_{22}O_3$  requires C, 77.4; H, 7.1%).

The ketones obtained by isomerisation of *p*-tolyl esters with 1.1 mols. of aluminium chloride for 2 hours at 160° were purified by steam distillation, crystallisation of the sodium salts, and subsequent distillation under reduced pressure.

3-n-Butyryl-p-cresol oxime forms needles, m. p. 96—97°, from light petroleum (Found : N, 7.3.  $C_{11}H_{15}O_2N$  requires N, 7.3%). 3-n-Butyryl-p-cresol phenylhydrazone separates from alcohol in rhombic prisms, m. p. 141—142° (Found : N, 10.15.  $C_{17}H_{20}ON_2$  requires N, 10.4%).

3-n-Valeryl-p-cresol (yield, 65%), made but not characterised by Wittig (*Annalen*, 1925, 446, 155), has b. p. 144—145°/15 mm. and separates from light petroleum in fine needles, m. p. 32—33° (Found : C, 74.9; H, 8.5.  $C_{12}H_{16}O_2$  requires C, 75.0; H, 8.3%). Its phenylhydrazone separates from alcohol in yellowish plates, m. p. 113—115° (Found : N, 9.7.  $C_{18}H_{22}ON_2$  requires N, 9.9%).

3-n-Hexoyl-p-cresol (yield, 80%), b. p. 150—152°/15 mm., crystallises from light petroleum in fine needles, m. p. 19° (Found : C, 75.3; H, 8.9.  $C_{13}H_{18}O_2$  requires C, 75.7; H, 8.7%). The phenylhydrazone separates from alcohol in platelets, m. p. 110—112° (Found : N, 9.2.  $C_{19}H_{24}ON_2$  requires N, 9.5%).

Although there is the possibility of the production of both 4- and 6-acyl-*m*-cresols in the isomerisation of *m*-tolyl esters, if the reaction is carried out at the ordinary temperature in nitrobenzene solution as described by Rosenmund the yield of the 6-compound

is negligible, being only 2% in the case of *m*-tolyl butyrate. The ketones of this class were purified by steam distillation, followed by distillation under reduced pressure.

4-*Propionyl-m-cresol oxime* separates from light petroleum in needles, m. p. 103–104° (Found: N, 7.7.  $C_{10}H_{13}O_2N$  requires N, 7.8%).

6-*n-Butyryl-m-cresol* separates from benzene in colourless plates, m. p. 97–98° (Found: C, 73.9; H, 7.8.  $C_{11}H_{14}O_2$  requires C, 74.2; H, 7.9%).

4-*n-Butyryl-m-cresol* (yield, 88%) has b. p. 142–144°/15 mm. and m. p. 17° (Found: C, 74.0; H, 7.6.  $C_{11}H_{14}O_2$  requires C, 74.2; H, 7.9%). Its *oxime* forms needles, m. p. 74–75°, from light petroleum (Found: N, 7.3.  $C_{11}H_{15}O_2N$  requires N, 7.3%). Its *phenylhydrazone* forms pale yellowish leaflets, m. p. 95–97°, from alcohol (Found: N, 10.2.  $C_{17}H_{20}ON_2$  requires N, 10.4%).

4-*n-Valeryl-m-cresol* (yield, 85%) has b. p. 152–154°/15 mm. and m. p. 16° (Found: C, 74.8; H, 8.2.  $C_{12}H_{16}O_2$  requires C, 75.0; H, 8.3%).

4-*n-Hexoyl-m-cresol* (yield, 93%), b. p. 162–164°/15 mm., separates from alcohol in prismatic needles, m. p. 23–24° (Found: C, 75.5; H, 8.8.  $C_{13}H_{18}O_2$  requires C, 75.7; H, 8.7%). Its *phenylhydrazone* separates from alcohol in leaflets, m. p. 92–93° (Found: N, 9.3.  $C_{19}H_{24}ON_2$  requires N, 9.5%).

4-*n-Heptoyl-m-cresol* (yield, 84%) has b. p. 172–174°/15 mm. and m. p. 18° (Found: C, 76.0; H, 9.1.  $C_{14}H_{20}O_2$  requires C, 76.4; H, 9.1%).

The best conditions for the preparation of 4-acylguaiacols were found to be as follows: Aluminium chloride (270 g.; 2 mols.) was dissolved in nitrobenzene (600 c.c.) by heating at 100°, the solution cooled to 10°, and the ester (1 mol.) added quickly; the solution, which was at first clear, changed to a very viscous mass. On gentle warming, hydrogen chloride was evolved and the viscous mass became micro-crystalline. After remaining at about 80° for  $\frac{1}{2}$ –1 hour, the product was kept over-night; the crystals were then collected out of contact with moist air and washed successively with benzene, benzene-light petroleum, and light petroleum.

The aluminium chloride compound was thus obtained as a cream-coloured sandy powder. It was added gradually to an excess of dilute hydrochloric acid; the almost pure 4-acylguaiacol then separated as an oil, which quickly solidified and was obtained in a yield of upwards of 50% of the theoretical. The nitrobenzene filtrate from the aluminium compound was distilled with steam to remove nitrobenzene and the remaining oil was distilled under diminished pressure; a further quantity of the 4-acylguaiacol was

thus obtained, followed at a temperature some 30° higher by the corresponding acylpyrocatechol.

The 4-acylguaiacols and 4-acylpyrocatechols are easily crystallisable compounds, the acylguaiacols being more soluble in organic solvents but less soluble in water than the corresponding acylpyrocatechols. The solubility of 4-acetylpyrocatechol in water is such as to render water unsuitable for its recrystallisation, but this solvent may very conveniently be employed for recrystallising 4-propionyl- and 4-*n*-butyryl-pyrocatechols, both of which are, with difficulty, soluble in benzene. 4-*n*-Valerylpyrocatechol and 4-*n*-hexoylpyrocatechol are easily soluble in hot benzene.

4-Acylguaiacols and acylpyrocatechols give green and very deep bluish-green colorations, respectively, with alcoholic ferric chloride. Certain constants of these compounds, with analyses, are given below :—

	M. p.	B. p. (15 mm.).	Found.		Formula.	Required.	
			% C.	% H.		% C.	% H.
4-Propionylguaiacol .....	61—62°	180—185°	66.5	6.6	C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	66.7	6.7
4- <i>n</i> -Butyryl .....	54—55	185—195	67.9	7.2	C <sub>11</sub> H <sub>14</sub> O <sub>3</sub>	68.0	7.2
4- <i>n</i> -Valeryl „ .....	60—62	195—197	69.0	7.6	C <sub>12</sub> H <sub>16</sub> O <sub>3</sub>	69.2	7.7
4- <i>n</i> -Hexoyl „ .....	60—62	212—215	70.1	8.1	C <sub>13</sub> H <sub>18</sub> O <sub>3</sub>	70.3	8.1
4- <i>n</i> -Valerylpyrocatechol	143—144	230—240	68.0	7.0	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub>	68.0	7.2
4- <i>n</i> -Hexoyl „	93—94	240—250	69.1	7.6	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub>	69.2	7.7

4-Propionylpyrocatechol and 4-*n*-butyrylpyrocatechol had b. p. 210—220° and 220—230°/15 mm. respectively. The m. p. of each was identical with that given by Rosenmund and Lohfert (*Ber.*, 1928, 61, 2601).

The following derivatives of the acylguaiacols have been prepared :—

4-Propionylguaiacyl benzoate, m. p. 108—110° (Found : C, 71.6; H, 5.8. C<sub>17</sub>H<sub>16</sub>O<sub>4</sub> requires C, 71.8; H, 5.6%). 4-Propionylguaiacol *p*-nitrophenylhydrazone, yellowish needles, m. p. 151—152°, from alcohol (Found : N, 13.3. C<sub>16</sub>H<sub>17</sub>O<sub>4</sub>N<sub>3</sub> requires N, 13.3%). 4-*n*-Butyrylguaiacyl benzoate, m. p. 75—77° (Found : C, 72.0; H, 6.0. C<sub>18</sub>H<sub>18</sub>O<sub>4</sub> requires C, 72.5; H, 6.0%). 4-*n*-Butyrylguaiacol phenylhydrazone, pale yellow needles, m. p. 91—92°, from dilute alcohol (Found : N, 9.6. C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>N<sub>2</sub> requires N, 9.9%). 4-*n*-Valerylguaiacyl benzoate, m. p. 85—87° (Found : C, 73.0; H, 6.3. C<sub>19</sub>H<sub>20</sub>O<sub>4</sub> requires C, 73.1; H, 6.4%). 4-*n*-Hexoylguaiacyl benzoate, m. p. 54—55° (Found : C, 73.4; H, 6.8. C<sub>20</sub>H<sub>22</sub>O<sub>4</sub> requires C, 73.6; H, 6.7%).

(3) *Isomerisation of Esters with Zinc Chloride.*—(a) Phenyl acetate (100 g.) and powdered zinc chloride (15 g.) were heated at 125° for 3 hours. The product gave *o*-acetylphenol (4 g.; yield, 4%) and *p*-acetylphenol (8 g.; yield, 8%).

(b) *m*-Tolyl propionate (75 g.) and powdered zinc chloride (37.5 g.) were heated at 150—160° for 1 hour. The product was dissolved

in dilute hydrochloric acid and distilled with steam. Extraction of the distillate with ether and distillation of the extract under low pressure gave 15 g. of pure 4-propionyl-*m*-cresol (yield, 20%).

(c) To guaiacyl acetate (20 g.) at 200°, powdered zinc chloride (5 g.) was added. Vigorous ebullition took place, and after 1 minute the melt was poured into water and boiled with dilute hydrochloric acid. Ether then extracted an oil, which was distilled under reduced pressure. A fraction, b. p. 180—200°/15 mm., solidified on cooling, and after crystallisation from benzene gave acetovanillone (5 g.), m. p. 113—114° (yield, 25%).

(4) *Condensation of Guaiacol with Fatty Acids by Means of Phosphorus Oxychloride*.—Guaiacol (100 g.) and glacial acetic acid (200 g.) were mixed, and phosphorus oxychloride (200 g.) was added slowly. After being warmed gently on the steam-bath until the evolution of hydrogen chloride ceased (3 hours), the product was poured into water, and the guaiacol distilled with steam. The non-volatile oil was extracted with ether and distilled under diminished pressure. The fraction, b. p. 180—200°/15 mm., solidified, and after crystallisation from benzene gave isoacetovanillone (26 g.), m. p. 91—92° (yield, 20%) (Found: C, 65.4; H, 6.3. Calc.: C, 65.1; H, 6.1%). It crystallised from water in long needles (m. p. 59—60°) containing water of crystallisation (Schneider and Kraft, *loc. cit.*, gave m. p. 91°, and 66—69° for the hydrate). isoAcetovanillone phenylhydrazone melts at 102° (Found: N, 10.8.  $C_{15}H_{16}O_2N_2$  requires N, 10.9%), and isoacetovanillone benzoate at 141—142° (Found: C, 70.7; H, 5.3.  $C_{16}H_{14}O_4$  requires C, 71.1; H, 5.2%).

5-Propionylguaiacol was prepared similarly (yield, 25%). It melts at 93—94°, and is moderately easily soluble in hot water or benzene (Found: C, 66.4; H, 6.7.  $C_{10}H_{12}O_3$  requires C, 66.7; H, 6.77%). The benzoate melts at 96—98° (Found: C, 71.6; H, 5.8.  $C_{17}H_{16}O_4$  requires C, 71.8; H, 5.6%).

5-*n*-Butyrylguaiacol, prepared similarly, melts at 81—82° (Found: C, 67.9; H, 7.2.  $C_{11}H_{14}O_3$  requires C, 68.0; H, 7.2%).

#### *Reduction of Acylphenols to Alkylphenols.*

For the conversion of the carbonyl group into the methylene group in the series of hydroxyketones, the usual procedure was to boil the ketone (1 part) under reflux on the steam-bath for 12—20 hours with amalgamated zinc (3 parts) and dilute hydrochloric acid (1:1) (6 parts) to which alcohol (2 parts) had been added. (When *o*-hydroxyketones were being reduced, the end of the reaction was clearly indicated by the failure of the colour reaction with ferric chloride.) The alcohol was removed by distillation with steam and the lower phenols were separated by continued distillation with

steam, but the rate of distillation became too slow with the higher members of the series to permit of their being separated by this method. They were therefore extracted from the reaction mixture, distilled in a vacuum, and recrystallised wherever possible from light petroleum. The following table shows the new phenols which were prepared and certain constants and analytical data :—

Phenol.	B. p. (15 mm.).	M. p.	Found.		Formula.	Calc.	
			% C.	% H.		% C.	% H.
<i>p</i> - <i>n</i> -Hexylphenol .....	155°	29°	80.8	10.1	C <sub>12</sub> H <sub>18</sub> O	80.9	10.1
<i>o</i> - <i>n</i> -Heptyl " .....	163—165	—	80.9	10.5	C <sub>13</sub> H <sub>20</sub> O	81.3	10.4
<i>p</i> - <i>n</i> -Heptyl " .....	165	24	81.2	10.3	C <sub>13</sub> H <sub>20</sub> O	81.3	10.4
3- <i>n</i> -Butyl- <i>o</i> -cresol .....	117—119	14	80.3	9.7	C <sub>11</sub> H <sub>16</sub> O	80.4	9.8
5- <i>n</i> -Butyl " .....	127—129	24	80.1	10.1	C <sub>11</sub> H <sub>16</sub> O	80.4	9.8
3- <i>n</i> -Amyl " .....	127—129	32	80.5	10.3	C <sub>12</sub> H <sub>18</sub> O	80.9	10.1
5- <i>n</i> -Amyl " .....	137—139	28	80.6	10.2	C <sub>12</sub> H <sub>18</sub> O	80.9	10.1
3- <i>n</i> -Hexyl " .....	139—141	8	80.9	10.5	C <sub>13</sub> H <sub>20</sub> O	81.3	10.4
5- <i>n</i> -Hexyl " .....	147—149	5	81.4	10.7	C <sub>13</sub> H <sub>20</sub> O	81.3	10.4
4- <i>n</i> -Butyl- <i>m</i> -cresol .....	132—134	18	80.5	9.9	C <sub>11</sub> H <sub>16</sub> O	80.4	9.8
4- <i>n</i> -Amyl " .....	137—139	24	80.6	10.2	C <sub>12</sub> H <sub>18</sub> O	80.9	10.1
4- <i>n</i> -Hexyl " .....	147—149	17	81.5	10.6	C <sub>13</sub> H <sub>20</sub> O	81.3	10.4
4- <i>n</i> -Heptyl " .....	153—155	24	81.3	10.8	C <sub>14</sub> H <sub>22</sub> O	81.6	10.7
3- <i>n</i> -Butyl- <i>p</i> -cresol .....	124—126	19	80.3	9.7	C <sub>11</sub> H <sub>16</sub> O	80.4	9.8
3- <i>n</i> -Amyl " .....	135—137	10	80.5	10.3	C <sub>12</sub> H <sub>18</sub> O	80.9	10.1
3- <i>n</i> -Hexyl " .....	143—150	30	81.0	10.5	C <sub>13</sub> H <sub>20</sub> O	81.3	10.4
5-Ethylguaiaacol .....	130—132	35—36	71.2	8.0	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub>	71.1	7.9
5- <i>n</i> -Propyl " .....	132—134	21—22	72.1	8.3	C <sub>10</sub> H <sub>14</sub> O <sub>2</sub>	72.3	8.4
4- <i>n</i> -Amyl " .....	155—157	—	74.0	9.3	C <sub>13</sub> H <sub>18</sub> O <sub>2</sub>	74.2	9.3
4- <i>n</i> -Hexyl " .....	165—167	—	74.7	9.6	C <sub>14</sub> H <sub>20</sub> O <sub>2</sub>	75.0	9.6

A number of the phenols prepared in the course of this work were known previously, but had not been obtained crystalline, namely, *p*-*n*-butylphenol, m. p. 12°; *p*-*n*-amylphenol, m. p. 18°; 4-*n*-propyl-*m*-cresol, m. p. 16°; and 4-*n*-propylguaiaacol, m. p. 16°. *p*-*n*-Propylphenol had m. p. 24°; Clemmensen (*Ber.*, 1914, 47, 51) gives m. p. 21—22°. Aqueous solutions of sodium *o*- and *p*-butylphenoxides are colourless, contrary to the statements of Read and Mullen (*J. Amer. Chem. Soc.*, 1928, 50, 1764). 4-*n*-Butylguaiaacol, prepared by the reduction of 4-*n*-butyrylguaiaacol, had b. p. 140—142°/15 mm. and its benzoate had m. p. 91.5°; Nomura and Hotta (*loc. cit.*) give b. p. of the reduction product of zingerone as 141—142°/13.5 mm. and m. p. of its benzoate as 92—93°.

The following benzoates of the above phenols are new :—

Benzoate.	M. p.	Found.		Formula.	Calc.	
		% C.	% H.		% C.	% H.
<i>p</i> - <i>n</i> -Propylphenyl .....	37—38°	79.6	6.8	C <sub>16</sub> H <sub>18</sub> O <sub>2</sub>	80.0	6.7
<i>p</i> - <i>n</i> -Butylphenyl .....	24—25	80.1	7.0	C <sub>17</sub> H <sub>18</sub> O <sub>2</sub>	80.3	7.1
<i>p</i> - <i>n</i> -Hexylphenyl .....	24	80.4	7.9	C <sub>19</sub> H <sub>22</sub> O <sub>2</sub>	80.8	7.8
<i>p</i> - <i>n</i> -Heptylphenyl .....	32—33	80.6	8.3	C <sub>20</sub> H <sub>24</sub> O <sub>2</sub>	81.0	8.1
4-Ethylguaiaacyl .....	58—59	74.7	6.3	C <sub>16</sub> H <sub>18</sub> O <sub>3</sub>	75.0	6.2
5-Ethylguaiaacyl .....	53	74.8	6.4	C <sub>16</sub> H <sub>18</sub> O <sub>3</sub>	75.0	6.2
4- <i>n</i> -Hexylguaiaacyl .....	82—83	76.8	7.9	C <sub>20</sub> H <sub>24</sub> O <sub>3</sub>	76.9	7.7

We desire to thank Mr. C. A. Hill of Boots Analytical Department for carrying out many of the analyses recorded in this paper.

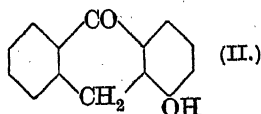
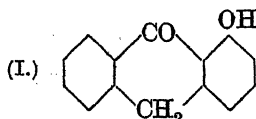
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NOTTINGHAM.

[Received, December 27th, 1929.]

# XLIV.—*Reduction Products of the Hydroxyanthraquinones. Part XI.*

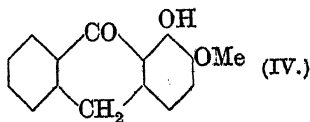
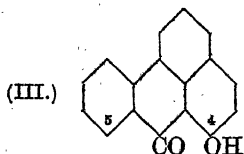
By EDWIN JOHN CROSS and ARTHUR GEORGE PERKIN.

WHEN unsymmetrical hydroxyanthraquinones are reduced, in general only one of the two theoretically possible hydroxyanthranols is produced; *e.g.*, 1-hydroxyanthraquinone yields 1-hydroxyanthranol (or anthrone) (I), there being no evidence of the simultaneous formation of the 4-hydroxy-compound (II).



The anthrone formula, which is applicable to 1-hydroxyanthranol (Meyer and Sander, *Annalen*, 1920, **420**, 113) and possibly to other 1-hydroxyanthranols, is adopted in all cases throughout this paper for the sake of simplicity.

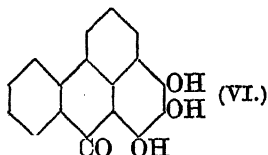
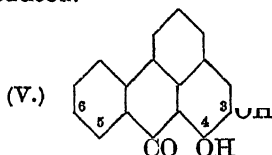
Although hitherto it has not been possible to speculate with any certainty as to the influence of the hydroxyl group or groups of hydroxyanthraquinones in definite positions on the production therefrom of this or that isomeric hydroxyanthranol, a determination of the exact structure of the latter has added considerably to our knowledge in this respect. For this purpose the conversion of hydroxyanthranol into hydroxybenzanthrone has been mainly studied, and the presence or absence of the  $\alpha$ -hydroxyl group in the latter ascertained by the employment of methyl iodide and alkali. Thus, when the hydroxybenzanthrone (III) derived from (I) is so treated, methylation does not occur, giving evidence that the former is, without doubt, the 4- or 5-hydroxy-compound (III), and the latter the 1-hydroxy-compound (Perkin and Spencer, *J.*, 1922, **121**, 474).



Although alizarin had hitherto been known to give but one anthranol (3:4-dihydroxyanthranol), Miller and Perkin (*J.*, 1925, **127**, 2684), employing stannous chloride and hydrochloric acid,



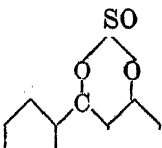
obtained from alizarin 2-methyl ether a mixture of 4-hydroxy-3-methoxy- and 1-hydroxy-2-methoxy-anthranol (IV). The constitution of the latter became evident from the fact that, by treatment with glycerol and sulphuric acid, *isobenzalizarin* (3:4- or 5:6-dihydroxybenzanthrone) (V) is obtained, a compound from which, by the reagents stated, only a monomethyl ether can be produced.



Adopting the same methods, it has been shown by Cross and Perkin (J., 1927, 1297) that the anthranols derived from anthrapurpurin, flavopurpurin, and anthragallol are respectively the 3:4:6-, 1:2:6-, and 1:2:3-trihydroxy-compounds, the last yielding 2:3:4-trihydroxybenzanthrone (VI).

The  $\alpha$ -hydroxyl group in hydroxybenzanthrones is not only resistant to methylation but is much less readily acetylated than the  $\alpha$ -hydroxyl of hydroxyanthraquinones: for instance, a fully acetylated derivative can be prepared from (V) only with difficulty, and from (VI), as yet, only a diacetyl compound has been obtained. Evidently, therefore, the chelate ring in  $\alpha$ -hydroxybenzanthrones possesses a much firmer character than that which is present in  $\alpha$ -hydroxyanthraquinones.

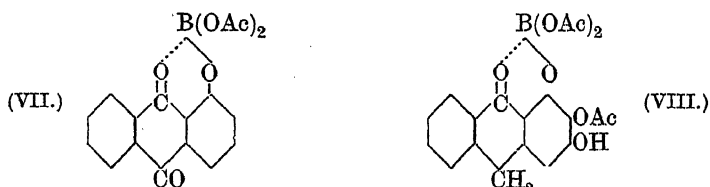
Green (J., 1927, 2341) suggests the employment of thionyl chloride as a reagent for the determination of the structure of hydroxy-anthranols, in that ortho- and peri-hydroxyls when present in a phenol yield thionyl derivatives, whereas such compounds are not given by meta- and para-dihydric phenols (J., 1924, 125, 1450; 1926, 1428, 2198; 1927, 500, 554). In order to illustrate the utility of this method, he examined only three anthranols, *viz.*, 1-hydroxy-anthranol (I), 4-chloro-1-hydroxyanthranol, and anthragallol-anthranol. Of these, the first two only yielded thionyl compounds,

evidently of the type , whereas the last did not so

react. From this scanty evidence, and notwithstanding the proof given by Cross and Perkin (*loc. cit.*) to the contrary, this author concludes that anthragallolanthranol is not the 1:2:3-trihydroxy-anthranol (1:2:3:9-tetrahydroxyanthracene) but the 2:3:4-

trihydroxyanthranol (1 : 2 : 3 : 10-tetrahydroxyanthracene). It appears at first sight somewhat strange that 1-hydroxyanthranol, which in reality is 1-hydroxyanthrone (Meyer and Sander, *loc. cit.*), reacts with thionyl chloride in the manner indicated, unless in these circumstances tautomerisation of the anthrone to the anthranol is presumed to occur.

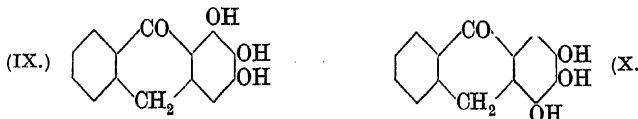
It has been shown by Dimroth and Faust (*Ber.*, 1921, 54, 3020) that when  $\alpha$ -hydroxyanthraquinones are treated with boroacetic anhydride, boric esters are produced. 1-Hydroxyanthraquinone thus yields 1-hydroxyanthraquinone boroacetate (VII), and diboroacetates are given by 1 : 4- and 1 : 5-dihydroxyanthraquinones.



The compounds are decomposed by water, giving  $\alpha$ -hydroxyanthraquinone and boric and acetic acids. The application of this method to  $\alpha$ -hydroxyanthranols (anthrones) was tested first with 1-hydroxy-2-methoxyanthrone: a boroacetate, however, could not be prepared, for, although with the boiling reagent chemical alteration evidently occurred, in the cold a product of an indefinite character resulted. Anthragallolanthranol at first gave substances of an indefinite character, and it was only by the employment of special conditions that success was attained. Though different preparations of the orange crystalline product varied somewhat in composition, there could be no doubt that they essentially consisted of a *boroacetic ester* of 1 : 3-dihydroxy-2-acetoxyanthranol (VIII), and this result further confirms the statement of Cross and Perkin (*loc. cit.*) that the anthranol prepared by the reduction of anthragallol itself is the 1 : 2 : 3-trihydroxy-compound (IX).

The fact that, with stannous chloride and hydrochloric acid, 2-ethylcarbonatoalizarin gives 1-hydroxy-2-ethylcarbonatoanthranol, apparently as sole product (Perkin and Story, J., 1929, 1405), suggested as desirable a study of the influence, if any, of the acyloxy-group in acyloxyanthraquinones on the orientation of the hydroxy- or acyloxy-groups in the anthranols derived therefrom by reduction. The method here adopted, which consists in adding stannous chloride-hydrochloric acid to a hot solution of the acyl compound in acetic acid, has given results of interest. From triacetylanthragallol, thus treated, two anthranols are obtained: (a) the 1 : 2 : 3-trihydroxy-compound (IX), present in but small amount, and (b)

the main product, which consists, as shown below, of the hitherto unknown 2 : 3 : 4-trihydroxy-9-anthranol (X).



As the acetoxy-group is so readily hydrolysed in the circumstances, it is remarkable that such a process can be applied to acetyl compounds. That the elimination of the acetyl group here only occurs when reduction is complete and not, at least to any extent, prior to this process in most instances, is due to the extreme rapidity of the latter reaction, for this in general occupies but a few seconds, though in practice a somewhat longer digestion has usually been employed. If stannous chloride-hydrochloric acid is added to a warm solution of the acetoxyanthraquinone in acetic acid and the mixture is kept without further heating, complete reduction usually occurs over-night.

In order to ascertain the constitution of (X), it was heated with glycerol and sulphuric acid, and there was thus obtained, with considerable difficulty and in small amount, a trihydroxybenzanthrone, here termed *benzanthragallol*. This compound, which differs considerably in properties from the *isobenzanthragallol* (VI) derived from 1 : 2 : 3-trihydroxy-9-anthranol, readily gives a *trimethyl* ether when treated with methyl iodide and alkali, whereas the isomeride does not. *Benzanthragallol*, therefore, has the constitution (XI), and can thus have only originated from the 2 : 3 : 4-trihydroxy-9-anthranol (X).



A complete proof is thus afforded that, on reduction, anthragallol itself gives 1 : 2 : 3-trihydroxy-9-anthranol, and not, as suggested by Green, the 2 : 3 : 4-trihydroxy-9- (or 1 : 2 : 3-trihydroxy-10-) anthranol. It is moreover evident that thionyl chloride is hardly a trustworthy reagent for the detection of the 1-hydroxyl group in hydroxyanthranols.

The reduction of 2 : 3-diacetylanthragallol in a similar manner was now studied, the result being the production of 1 : 2 : 3-trihydroxy-9-anthranol (IX) identical with that given by anthragallol itself.

In order to illustrate more clearly the effect of the acetyl and other groups in this connexion, the results of this section of the investigation are embodied in the following table, and here, for purposes of comparison, the reduction products given by the free hydroxyanthraquinones are also included.

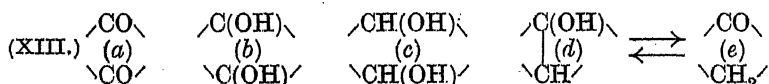
Anthraquinones.	Anthranols obtained by reduction.	
Anthragallol	1 : 2 : 3-Trihydroxy-9-anthranol	
Triacetylanthragallol	" "	2 : 3 : 4-Trihydroxy-9-anthranol
Diacetylanthragallol	" "	
Tribenzoylanthragallol		Dibenzoyl-2 : 3 : 4-tri-hydroxy-9-anthranol
Dibenzoylanthragallol	Dibenzoyl-1 : 2 : 3-tri-hydroxy-9-anthranol Monobenzoyl-1 : 2 : 3-tri-hydroxy-9-anthranol	
Triethylcarbonato-anthragallol	2 : 3-Diethylcarbonato-1-hydroxy-9-anthranol	Dicarbethoxy-2 : 3 : 4-tri-hydroxy-9-anthranol
Diethylcarbonato-anthragallol	" "	
	2-Ethylcarbonato-1 : 3-dihydroxy-9-anthranol	
Alizarin : (acid solution)	1 : 2-Dihydroxy-9-anthranol	3 : 4-Dihydroxy-9-anthranol
(alkaline solution)		" "
2-Acetylalizarin	" "	
Diacetylalizarin	" " (trace)	" "
Alizarin 2-methyl ether	1-Hydroxy-2-methoxy-9-anthranol	4-Hydroxy-3-methoxy-9-anthranol
Acetylalizarin 2-methyl ether		" "
1-Acetoxyanthraquinone		4-Hydroxy-9-anthranol
1 : 8-Dihydroxy-anthraquinone	1 : 8-Dihydroxy-9-anthranol	
1 : 8-Diacetoxy-anthraquinone		4 : 5-Dihydroxy-9-anthranol (XII)
1 : 2 : 6-Trihydroxy-anthraquinone	1 : 2 : 6-Trihydroxy-9-anthranol	

Although acetoxyanthraquinones are reduced very rapidly (*loc. cit.*) by the method here employed, the reduction of ethylcarbonatoanthraquinones (or at least of triethylcarbonatoanthragallol) occurs more slowly, because, though, in the circumstances employed, the carbethoxy-group is less readily eliminated than the acetyl group, it is apparent that, in the instance above cited, some hydrolysis with removal of the ethylcarbonato-group has taken place, both before and after the reduction. Thus, under the conditions employed (see above), triethylcarbonatoanthragallol (A) yields in part diethylcarbonatoanthragallol (B). (A) on reduction

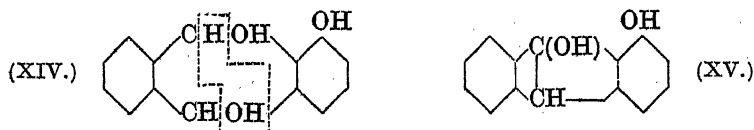
gives 2:3:4-*triethylcarbonatoanthrone*, passing by subsequent hydrolysis to the *diethyl* compound, whereas from (B) 1-*hydroxy-2:3-diethylcarbonatoanthrone* is obtained.

Among the points of interest indicated above are the preparation, not only of the two new hydroxyanthranols (II) and (X), but of 4-hydroxy-3-methoxy- and 1:2-dihydroxy-9-anthranols, compounds hitherto not readily obtained, in almost quantitative yield. That 1:2-dihydroxy-9-anthranol can also be prepared in this way directly from alizarin—though in conjunction with the 3:4-dihydroxy-compound—has also been ascertained for the first time, and this affords evidence that reduction of an  $\alpha$ -hydroxyanthraquinone in acid solution and in an alkaline medium does not of necessity proceed in an identical manner in both cases.

The results of this investigation indicate that when hydroxyanthraquinones containing an  $\alpha$ -hydroxy-group are reduced in an acid solution in the manner indicated, the  $\alpha$ -hydroxy-group as a rule is found to be in the 1-position adjacent to the carbonyl group, or to the hydroxyl in the 9-position of the resulting hydroxyanthrone or hydroxyanthranol. If, on the other hand, the  $\alpha$ -hydroxyl of the hydroxyanthraquinone is acylated before reduction, the reverse is the case, this hydroxyl then occupying the 4-position in the product. In other words, the carbonyl adjacent to the acyloxy-group in  $\alpha$ -acyloxyanthraquinones is preferably reduced: this is clearly shown by (I) and (II), which represent respectively the reduction products of 1-hydroxy- and 1-acetoxy-anthraquinone. If in these cases the reaction proceeds according to the usually accepted scheme (XIII), an explanation of the fact cited above, in the light of our present knowledge, is difficult, because it is in no way clear why, in the

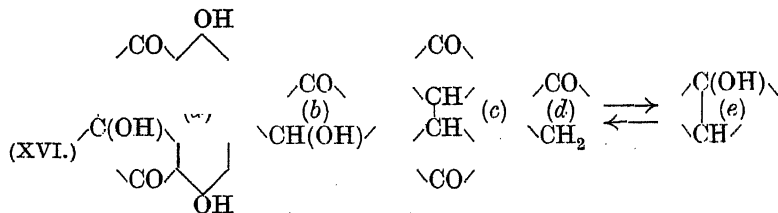


change of (XIV) into (XV) ( $c \rightarrow d$ ) during the reduction of 1-hydroxyanthraquinone to 1-hydroxyanthrone (or anthranol), water should be split off only in the manner indicated, and not in both directions



with the simultaneous formation of 1- and 4-hydroxyanthranols. It seems reasonable to infer that the influence dominating the formation of 1-hydroxyanthranols from  $\alpha$ -hydroxyanthraquinones by acid reduction is the chelate linkage between the  $\alpha$ -hydroxyl and

the carbonyl group of the latter. This renders the latter immune from reduction, a fact which can also be expressed by saying that the chelate linkage remains intact in the series of changes involved. Such a suggestion can be indicated (XVI) by the stages (a) dihydroxy-pinacol, (b) hydroxyanthranol, (c) dianthrone, (d) anthrone, (e) anthranol. On the other hand, when the  $\alpha$ -hydroxy-group is



acylated the chelate linkage is destroyed, and the adjacent carbonyl group is no longer immune from reduction. Of interest in this respect is the statement of Meyer and Sander (*loc. cit.*) that 1-hydroxy-9-anthranol is produced when 1-hydroxyanthraquinone is reduced in acid solution, and that only by the use of alkaline media could the corresponding anthranol be obtained. If the scheme outlined above is to be considered, at least in the main, correct, proof of the formation of hydroxydianthrone (stage c) during the reduction process is necessary, and though there have been indications during more recent work, in special instances, of the presence of such compounds in the final products, further investigation is necessary to determine if their formation in this manner from  $\alpha$ -hydroxyanthraquinones is of general occurrence.

An exception to the rule that  $\alpha$ -hydroxyanthraquinones yield on reduction 1-hydroxyanthrones (or anthranols) is the 1:2:7-trihydroxy-compound (anthrapurpurin) (*loc. cit.*), which gives both with stannous chloride-hydrochloric acid and with aqueous ammonia and zinc dust, 3:4:6-trihydroxy-9-anthranol. In the case of anthrapurpurin, however, two factors can be considered to influence the reaction: (a) the 1-hydroxy-group and (b) the remote  $\beta$ -hydroxy-group in the 7-position. Whereas it is to be anticipated that the former (compare alizarin) will tend, though only in part (*loc. cit.*), to give an  $\alpha$ -hydroxyanthrone, the latter (compare 2-hydroxy- and 2-acetoxy-anthraquinone, which, as experiment has shown, both yield 3-hydroxyanthranol as sole product) will desire to take up the 6-position in the resulting hydroxyanthranol. The latter influence evidently predominates in the present instance: this point will be further discussed in a subsequent communication.

In the German patent 187495 (Friedländer's "Fortschritte," IX,

816) two methods are given for the preparation of hydroxybenzanthrones: (a) the action of glycerol and sulphuric acid on hydroxyanthranols and (b) the similar treatment of hydroxyanthraquinones in the presence of reducing agents. That in these circumstances the product of the reduction, according to the patent, of a hydroxyanthraquinone and the anthranol derived therefrom by alkaline reduction, do not necessarily give the same hydroxybenzanthrone is obvious from the results of the present investigation, and indeed the properties given in the patent of the hydroxybenzanthrone derived from alizarin differ markedly from those of the 7:8-dihydroxy-compound (Perkin, J., 1920, 117, 702) which is obtained in a similar manner from 3:4-dihydroxyanthranol (deoxylizarin). Evidently, therefore, the former product is either 3:4- or 5:6-dihydroxybenzanthrone. Turski and Grynwasser (*Rocz. Chem.*, 1929, 9, 78) purport to have decided this point by synthetical methods and describe these compounds as melting at 285° and 185° respectively. Their paper\* is remarkable in that it consists merely of a series of statements. It contains no account of the properties or the melting points of the new compounds which were prepared for the purpose of these syntheses, and but one analysis seems to have been performed, the figures of which are not stated. The results of these authors, at least in regard to one or other of the dihydroxybenzanthrones they describe, are not in harmony with those of Miller and Perkin (*loc. cit.*), who obtained *isobenzalizarin* (V) from 1-hydroxy-2-methoxyanthranol; for this, which melts at 265°, is either the 3:4- or the 5:6-dihydroxy-compound. A reinvestigation has confirmed the correctness of the melting points previously given both for this compound and for its acetyl derivative (243—245°). The action of glycerol and sulphuric acid on alizarin in the presence of aniline sulphate was now studied, with the result that the crude product obtained resembled that described in the patent, more especially in regard to its giving strongly fluorescent solutions both in sulphuric acid and in dilute alkali. This substance is, however, a mixture, for on treatment by the method described below, a more sparingly soluble fraction can be isolated in small amount, which is devoid of fluorescent property. This yielded an acetyl compound melting at 243—245°, and without doubt consisted of *isobenzalizarin*. There is no reason why alizarin, in the circumstances, should not yield isomeric hydroxybenzanthrones, and if this is so, it is possible that the compound, m. p. 185°, described by Turski and Grynwasser as 5:6-dihydroxybenzanthrone, which gives fluorescent solutions in the manner indicated, is present in

\* For a translation of this paper, which is written in Polish, we are indebted to the kindness of Mrs. J. W. McLeod of Leeds.

the more soluble fraction of the reaction product. Should such be the case, then isobenzalazarin is 3 : 4-dihydroxybenzanthrone, and the nature of the compound they describe as melting at 285°, and to which they ascribe the same constitution, is not clear.

#### EXPERIMENTAL.

*Reduction of Triacetylanthrakgallol.*—To a boiling solution of triacetylanthrakgallol (10 g.) in acetic acid (100 c.c.), stannous chloride (40 g.) dissolved in warm hydrochloric acid (100 c.c.)\* was added. The pale yellow liquid darkened, became lighter when boiled for a short time, and deposited crystalline 2 : 3 : 4-trihydroxy-9-anthranol (X). After cooling, this was collected, washed with a mixture of acetic and hydrochloric acids and with water, and dried (yield, 4.3 g.). Addition of water to the filtrate gave a precipitate (1.5 g.) of which the colour reactions and the m. p. of the monoacetyl derivative, m. p. 239—240° (decomp.) (Breare and Perkin, J., 1923, 123, 2607), showed that it was 1 : 2 : 3-trihydroxy-9-anthrone (or anthranol). The total yield of anthranols (5.8 g.) represents 91.6% of the theoretical amount.

2 : 3 : 4-Triacetoxy-9-anthranyl acetate was readily obtained by digesting the 2 : 3 : 4-trihydroxy-compound with boiling acetic anhydride and pyridine for a short time and adding alcohol to the product after cooling. The crystals obtained formed colourless prisms, m. p. 199—201°, after recrystallisation from alcohol-acetic acid (Found : C, 64.2; H, 4.45;  $C_2H_4O_2$ , 58.3.  $C_{22}H_{18}O_8$  requires C, 64.4; H, 4.4;  $C_2H_4O_2$ , 58.5%).

2 : 3 : 4-Trihydroxy-9-anthranol can be obtained only in a crude condition and of a deep green colour when the acetyl compound is hydrolysed with hydrochloric acid in the usual manner. If, however, a solution of the acetyl compound in boiling acetic acid is digested with half its volume of stannous chloride-hydrochloric acid until crystals commence to separate, the anthranol is obtained in needles which have, at most, a pale greenish tint. When heated, it gradually darkens, does not melt below 300°, and at this temperature is greenish-black (Found : C, 69.4; H, 4.2.  $C_{14}H_{10}O_4$  requires C, 69.4; H, 4.1%). The possibility, suggested by its high melting point, that this compound might be a dianthrone rather than an anthrone (anthranol) was disproved by a molecular-weight determination of the tetra-acetyl compound by the cryoscopic method with naphthalene as solvent (Found :  $M$ , 400.  $C_{22}H_{18}O_8$  requires  $M$ , 410. As the colourless solution, which has a faint blue fluorescence, gradually darkens, the initial readings only are trustworthy).

\* This concentration of stannous chloride in hydrochloric acid was employed throughout the investigation.



2:3:4-Trihydroxy-9-anthranol gives in 10% aqueous sodium hydroxide an orange solution which becomes yellow and finally brown in air: in the same circumstances, 1:2:3-trihydroxy-9-anthranol gives an orange liquid which eventually develops a deep violet tint. Again, the latter in alcoholic solution gives with benzoquinone violet crystals of anthragallol dianthronequinone (Breare and Perkin, *loc. cit.*), but the 2:3:4-trihydroxy-compound is devoid of this characteristic. When oxidised with chromic acid in acetic acid solution, 2:3:4-triacetoxy-9-anthranyl acetate yielded orange crystals, m. p. 218—220°; these probably consisted of 2:3-diacetylanthragallol, as triacetylanthragallol was obtained from them by acetylation. Attempts to prepare a dianthrone from 2:3:4-trihydroxy-9-anthrone have been unsuccessful.

*Benzanthragallol*.—A mixture of 2:3:4-trihydroxy-9-anthranol (1 g.), sulphuric acid (8 c.c.), water (6 c.c.), and glycerol (2 g.) was heated with stirring to 120—125° during 20 minutes, and kept there for the same period. The product was poured into water, the washed precipitate dried and digested with alcohol, the concentrated solution poured into ether, and the ethereal solution well washed. Evaporation gave a brown residue, from which, by acetylation with acetic anhydride and pyridine, minute yellow crystals (0.05—0.07 g.) were obtained. These were again acetylated, crystallised from acetic acid, and, being still impure, hydrolysed with hydrochloric acid in the usual manner. The product was dissolved in alcohol, and boiling water added to the filtered solution, which caused the separation of small orange-yellow prisms. These gradually darkened above 200° and became black at about 290° without any sign of fusion (Found: C, 73.0; H, 3.8.  $C_{17}H_{10}O_4$  requires C, 73.4; H, 3.6%). This substance, *benzanthragallol*, dissolves in sulphuric acid with a crimson, and in 1% caustic soda solution with a violet colour which quickly fades to a yellow tint in air. With 10% caustic soda solution, a deep blue colour is obtained which becomes green and then yellow in air. *Benzanthragallol* dyes mordanted woollen cloth in shades distinct from those given by anthragallol and by *isobenzanthragallol*, although they approximate in depth to those given by the former colouring matter. Orange, orange-brown, red-brown, and dark brown shades are given by tin, aluminium, chromium, and iron mordants respectively.

*Triacetylbenzanthragallol*, prepared in the usual manner, gives a fluorescent solution in acetic acid and crystallises therefrom in pale yellow needles, m. p. 221—223° (Found: C, 68.3; H, 4.1;  $C_{17}H_{10}O_4$ , 68.5.  $C_{23}H_{16}O_7$  requires C, 68.3; H, 4.0;  $C_{17}H_{10}O_4$ , 68.8%).

*Methylation*. To a boiling mixture of triacetylbenzanthragallol

(0.5 g.) in methyl alcohol (7.5 c.c.) and methyl iodide (3 c.c.), caustic potash (0.5 g.) \* in methyl alcohol was added during 12 hours. The product was concentrated, poured into ether, insoluble resinous matter removed, and the ethereal solution washed with dilute alkali and evaporated. The residue, crystallised first from benzene and then from alcohol, yielded lemon-yellow, hair-like needles (0.07 g.), m. p. 143—144° (Found : C, 74.6; H, 5.1; CH<sub>3</sub>, 13.9. C<sub>20</sub>H<sub>16</sub>O<sub>4</sub> requires C, 75.0; H, 5.0; CH<sub>3</sub>, 14.1%). *Benzanthragallol trimethyl ether* can also be prepared by methylating benzanthragallol with methyl sulphate in the usual manner. Its yellow ethereal and alcoholic solutions have a green fluorescence.

*Reduction of 2 : 3-Diacetylanthragallol.*—On treatment of this compound with stannous chloride—hydrochloric acid by a similar method to that employed with triacetylanthragallol, only 1 : 2 : 3-trihydroxy-9-anthrone (or anthranol) was produced.

*Tribenzoylanthragallol.*—Dibenzoylanthragallol (see below) (2 g.), dissolved in pyridine (6 c.c.), was treated with benzoyl chloride (1 c.c.); crystals (2.3 g.) separated, and after dilution with an equal volume of alcohol these were removed and recrystallised from benzene—alcohol, pale yellow prisms, m. p. 213—215°, being obtained (Found : C, 73.8; H, 3.35. C<sub>35</sub>H<sub>20</sub>O<sub>8</sub> requires C, 73.9; H, 3.5%).

*Reduction.* To *tribenzoylanthragallol* (1 g.) in boiling acetic acid (50 c.c.), a boiling solution of stannous chloride—hydrochloric acid (25 c.c.) was added; the green precipitate first formed became colourless and crystalline after a few minutes' boiling. When cool, the crystals (0.5 g.) were removed (filtrate A), washed with hydrochloric acid and water, and recrystallised from acetone, almost colourless prisms containing acetone of crystallisation being obtained. When freed from solvent of crystallisation, these melted at 212—214° (Found : C, 74.4; H, 4.1; C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>, 55.6. C<sub>28</sub>H<sub>18</sub>O<sub>6</sub> requires C, 74.7; H, 4.0; C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>, 54.2%). A further quantity of this substance was isolated from filtrate A by dilution with water; the precipitate was collected, washed with hydrochloric acid and water, dried, and dissolved in boiling alcohol, from which crystals (0.25 g.) separated on cooling.

In order to eliminate the benzoyl groups from this compound, *dibenzoyl-2 : 3 : 4-trihydroxy-9-anthrone* (or *anthranol*), it was suspended in methyl alcohol, caustic soda solution added in small amount, and the mixture boiled for a few seconds. Acidification now yielded a dark purple precipitate, which was extracted with sodium bicarbonate solution to remove benzoic acid, dried, and acetylated. The product, repeatedly crystallised from alcohol—

\* Commercial stick. Theory requires 0.415 g. KOH for hydrolysis of the acetoxy-groups and formation of the trimethyl ether.

acetic acid, was obtained as colourless prisms, identical (mixed melting point) with 2 : 3 : 4-triacetoxy-9-anthranyl acetate.

*Dibenzoylanthragallol*.—Benzoyl chloride (2.3 c.c.) was slowly added to anthragallol (2 g.) in pyridine (10 c.c.) and after a while the solution was diluted with alcohol (10 c.c.). Crystals (2.5 g.) separated, and on recrystallisation from benzene were obtained as yellow leaflets, m. p. 204—206°. As this melting point is very similar to that of tribenzoylanthragallol (m. p. 213—215°), a determination of the molecular weight was necessary (Found : C, 72.4; H, 3.6; *M*, 453.  $C_{28}H_{16}O_7$  requires C, 72.4; H, 3.45%; *M*, 464).

*Reduction*. To a boiling solution of *dibenzoylanthragallol* (1 g.) in acetic acid (60 c.c.), stannous chloride—hydrochloric acid (20 c.c.) was added slowly in order to avoid precipitation and the mixture was boiled for 5 minutes. On cooling, crystals (0.6 g.) were gradually deposited (filtrate A); these were washed with hydrochloric acid and then with water, and recrystallised from acetic acid, very pale yellow needles, m. p. 188—190°, being obtained (Found : C, 74.8; H, 4.0.  $C_{28}H_{18}O_8$  requires C, 74.7; H, 4.0%).

This substance, *dibenzoyl-1 : 2 : 3-trihydroxyanthrone* (or *anthranol*), suspended in boiling alcohol, was treated with a few drops of caustic soda solution (10%). The deep yellow liquid first formed quickly became brown and from this by acidification and dilution with water a dark violet precipitate separated. This was collected, extracted with sodium bicarbonate solution to remove benzoic acid, and acetylated with a mixture of equal parts of acetic anhydride and acetic acid. Crystals separated as the boiling proceeded, and these, which after recrystallisation from much acetic acid melted at 239—240° (decomp.), consisted without doubt (mixed melting point) of monoacetyl-1 : 2 : 3-trihydroxyanthrone (or anthranol).

From the filtrate (A), on dilution with water, a precipitate (0.2 g.) separated. This, repeatedly crystallised from alcohol—acetic acid, gave colourless plates, m. p. 213—216° (decomp.) (Found : C, 72.7; H, 4.2.  $C_{21}H_{14}O_5$  requires C, 72.8; H, 4.05%). As this compound on alkaline hydrolysis yielded an anthranol having the characteristic properties of the 1 : 2 : 3-trihydroxy-compound, it was evidently *monobenzoyl-1 : 2 : 3-trihydroxyanthrone* (or *anthranol*).

*Triethylcarbonatoanthragallol*.—Diethylcarbonatoanthragallol (Perkin and Storey, J., 1928, 242) (6 g.) was dissolved in a mixture of pyridine (3 c.c.) and benzene (60 c.c.) and, after partial cooling, ethyl chloroformate (12 c.c.) was added all at once to the stirred solution. Viscid matter was gradually deposited, and after addition of charcoal the mixture was boiled, and the liquid filtered and evaporated to dryness with stirring. The residue, after being

washed with alcohol, crystallised from alcohol-acetic acid in very pale yellow prisms (5.9 g.), m. p. 103—105° (Found: C, 58.4; H, 4.3.  $C_{23}H_{20}O_{11}$  requires C, 58.5; H, 4.2%).

If a suspension of *triethylcarbonatoanthragallol* in cold pyridine is kept over-night, it is converted without apparent solution into the diethylcarbonato-derivative. Tribenzoylanthragallol is, however, not thus affected. Diethylcarbonatoanthragallol is again produced when a cold acetic acid solution of the triethylcarbonato-compound is treated with stannous chloride-hydrochloric acid, and the mixture kept over-night. This accounts for the fact (see below) that, when triethylcarbonatoanthragallol is reduced in the manner indicated, the products are identical with those given by the diethylcarbonato-derivative.

*Reduction.* To a boiling solution of triethylcarbonatoanthragallol (4 g.) in acetic acid (40 c.c.), a boiling solution of stannous chloride-hydrochloric acid (40 c.c.) was added. The precipitate first formed rapidly redissolved and the deep orange solution gradually became pale yellow. After 2 days, the crystals (0.9 g.) (filtrate A) were removed and recrystallised from alcohol-acetic acid, pale yellow prisms, m. p. 131—132°, being obtained (Found: C, 62.4; H, 4.9.  $C_{20}H_{18}O_8$  requires C, 62.2; H, 4.7%).

The removal of the carbethoxy-groups from this compound, which evidently consisted of 1-hydroxy-2:3-diethylcarbonato-9-anthranol, and the acetylation of the product were carried out as with dibenzoyl-1:2:3-trihydroxyanthranol, monoacetyl-1:2:3-trihydroxy-9-anthranol being obtained.

Addition of water to filtrate (A), which had a strong odour of ethyl acetate, gave a resinous precipitate. This, after being washed, was dissolved in a little alcohol; the crystals (1 g.) obtained, on recrystallisation from alcohol, yielded colourless needles, m. p. 156—158° (Found: C, 62.1; H, 4.8.  $C_{20}H_{18}O_8$  requires C, 62.2; H, 4.7%). As this substance gave 2:3:4-triacetoxy-9-anthranyl acetate by alkaline hydrolysis and subsequent acetylation, it consisted of *dicarbethoxy-2:3:4-trihydroxy-9-anthranol* (or *anthrone*).

*Diethylcarbonatoanthragallol.*—The method employed for the preparation of this compound differed somewhat from that given by Perkin and Storey (*loc. cit.*). To anthragallol (5 g.) in hot pyridine (20 c.c.), ethyl chloroformate (6.5 c.c.) was slowly added, followed, after cooling, by alcohol; the crystals obtained melted at 174—175° after recrystallisation from acetic acid.

*Reduction.* A boiling solution of stannous chloride-hydrochloric acid (120 c.c.) was added to diethylcarbonatoanthragallol (6 g.) in boiling acetic acid (120 c.c.). Next day, the crystals (2.4 g.) which had separated were collected (filtrate A) and repeatedly crystallised

from alcohol-acetic acid. The product was identical with the diethylcarbonato-1 : 2 : 3-trihydroxy-9-anthrone (mixed melting point) prepared in part (see above) by the reduction of triethylcarbonatoanthragallol.

From the filtrate (A) by addition of water a precipitate was obtained which, when digested with alcohol, yielded crystals (1 g.); these, recrystallised from acetic acid, gave almost colourless prisms, m. p. 218—219° (decomp.) (Found: C, 64.9; H, 4.7.  $C_{17}H_{14}O_6$  requires C, 65.0; H, 4.5%). Alkaline hydrolysis gave 1 : 2 : 3-trihydroxy-9-anthrone (or anthranol)—evidence that the compound was its *monocarbethoxy*-derivative. From the alcoholic filtrate, only resinous matter could be isolated.

*Reduction of Monoacetylalizarin.*—To monoacetylalizarin (5 g.) in boiling acetic acid (50 c.c.), boiling stannous chloride-hydrochloric acid (50 c.c.) was added, and the digestion continued for a few minutes. The mixture slowly deposited pale orange plates of 1 : 2-dihydroxyanthrone (3 g.), which, after recrystallisation from alcohol, melted at 149—151° (Found: C, 74.7; H, 4.7. Calc. for  $C_{14}H_{10}O_3$ : C, 74.3; H, 4.4%). Acetylation in the usual manner gave 1 : 2-diacetoxy-9-anthranyl acetate, which crystallised from alcohol-acetic acid in colourless plates, m. p. 185—187° (Found: C, 68.1; H, 4.8.  $C_{20}H_{16}O_6$  requires C, 68.2; H, 4.5%).

The filtrate from the reduction mixture gave a further 0.4 g. of 1 : 2-dihydroxyanthrone on addition of water.

*Reduction of Diacetylalizarin.*—Stannous chloride-hydrochloric acid (50 c.c.) was added to diacetylalizarin (5 g.) in boiling acetic acid (50 c.c.), and the mixture boiled for a few minutes. The liquid, at first orange-red, soon became lighter in colour and, on keeping, deposited orange needles consisting apparently of the oxonium salt. These were removed (filtrate A) and decomposed by digestion with boiling water, yielding a pale yellow product (2.35 g.) which was shown to be deoxyalizarin by the melting point of its acetyl compound in admixture with acetyldeoxyalizarin.

The filtrate A, on dilution with water, gave a precipitate (0.35 g.) (filtrate B) of 1 : 2-dihydroxyanthrone, identified in the form of its acetyl derivative, m. p. 185—187°.

From the filtrate B, by saturation with sodium chloride, a further amount (0.65 g.) of deoxyalizarin was isolated.

*Reduction of Acetylalizarin 2-Methyl Ether.*—A solution of the ether (30 g.) in boiling acetic acid (300 c.c.) was slightly cooled, and stannous chloride-hydrochloric acid (120 c.c.) then added. An orange precipitate immediately separated which became crystalline and lighter in colour on keeping. After 60 hours, the crystals (22 g.) were collected: they consisted, without doubt, of 4-hydroxy-

3-methoxyanthranol (Miller and Perkin, *loc. cit.*). From the acid filtrate, a trifling amount of the same compound could be isolated.

*Reduction of Alizarin.*—To a boiling solution of alizarin (2 g.) in acetic acid (100 c.c.), hot stannous chloride–hydrochloric acid (100 c.c.) was added and the mixture was boiled for a few minutes and then diluted with an equal volume of boiling water. On cooling, crystals (0.8 g.) of 1:2-dihydroxyanthrone separated; after recrystallisation from alcohol, they melted at 149–151°. The filtrate was further diluted with water and saturated with sodium chloride, the precipitate collected and dissolved in a little alcohol, and the solution treated with boiling water. On cooling, crystals (0.5 g.) separated having all the properties of 3:4-dihydroxy-anthranol.

When alizarin is digested with stannous chloride–hydrochloric acid in the absence of acetic acid (compare Goodall and Perkin, J., 1924, 125, 473), a viscid mass is obtained, reduction, at least in part, proceeding beyond the anthranol stage. From the product, which is readily soluble in alcohol, only 3:4-dihydroxy-9-anthranol in trifling amount has hitherto been isolated.

*Reduction of 1-Acetoxyanthraquinone.*—To 1-acetoxyanthraquinone (2 g.) in hot acetic acid (15 c.c.), stannous chloride–hydrochloric acid (12 c.c.) was added, causing a deposit to separate (stage A). This, on further heating, yielded an orange-brown liquid, which rapidly became pale yellow and then deposited crystals. These were collected after 12 hours and recrystallised, first from acetic acid containing stannous chloride–hydrochloric acid, and then from toluene. The almost colourless, flat needles of 4-hydroxy-9-anthranol obtained melted at 240–242°. If the mixture at stage A is kept in the cold for 2 days, complete conversion into the anthranol also occurs without further heating (Found: C, 79.7; H, 4.9.  $C_{14}H_{10}O_2$  requires C, 80.0; H, 4.8%). From the reduction mother-liquors, a trace of the same compound only could be isolated, and there was no evidence of the formation of the isomeric 1-hydroxy-9-anthrone. *Acetyl-4-hydroxy-9-anthranol*, prepared in the usual manner, forms colourless prisms, m. p. 173–175°. The alcoholic solution has a faint blue fluorescence (Found: C, 73.4; H, 4.7.  $C_{18}H_{14}O_4$  requires C, 73.5; H, 4.8%).

*Reduction of Diacetylchrysazin.*—To diacetylchrysazin (4.5 g.) in boiling acetic acid (150 c.c.), stannous chloride–hydrochloric acid (100 c.c.) was added. The crystals which separated on cooling were collected (yield, 3.5 g.) and crystallised from alcohol or nitrobenzene, from which solvents 4:5-dihydroxy-9-anthranol separated in almost colourless leaflets or prismatic needles respectively. These darkened

at 250° and melted at about 293—295° (Found: C, 74.0; H, 4.6.  $C_{14}H_{10}O_3$  requires C, 74.3; H, 4.4%).

*Acetyl-4:5-dihydroxy-9-anthranol* crystallises from acetic anhydride in needles, m. p. 220—222°, which gradually develop a brownish-black tint on exposure to sunlight (Found: C, 67.7; H, 4.5.  $C_{20}H_{16}O_6$  requires C, 68.2; H, 4.5%). Sulphuric acid dissolves it to form a brown liquid which slowly becomes green and finally orange.

*Reduction of 2-Acetoxyanthraquinone.*—To 2-acetoxyanthraquinone (2 g.) in acetic acid (15 c.c.), stannous chloride–hydrochloric acid (15 c.c.) was added, and the solution boiled for 5 minutes. The crystals which separated on cooling melted at 198—200° and evidently consisted of 3-hydroxy-9-anthranol, for on acetylation the acetyl compound, m. p. 155—157°, was produced. A further amount of the same substance was contained in the reduction mother-liquor, from which also the acetyl compound was prepared.

*Formation of isoBenzalizarin from Alizarin.*—A mixture of alizarin (5 g.), sulphuric acid (62° Bé; 125 g.), glycerol (10 g.), and aniline sulphate (7.5 g.) was gradually heated to 150° and kept there for 1 hour. The liquid, when poured into water, gave a green precipitate; this was dried and dissolved in alcohol and the solution was concentrated and poured into much ether. From the residue obtained by evaporation of the ether, only unchanged alizarin could be isolated. Better results were obtained by first heating the solution of alizarin and aniline sulphate at 150° for an hour, then adding the glycerol and heating again for an hour. The product, isolated with ether as above stated, gave on acetylation a small quantity of an acetyl compound, m. p. 243—245°, identical with monoacetylisobenzalizarin (mixed melting point).

*2-Acetylanthragallol Boroacetate.*—1:2:3-Trihydroxy-9-anthrone (1 g.) in cold acetic anhydride (6 c.c.) was treated with boroacetic anhydride (0.15 g.) and a few drops of pyridine, and the mixture kept over-night. The anthranol, without apparent solution, was converted into a dull orange, crystalline powder; this was collected, washed with acetic anhydride and with anhydrous ether, and centrifuged until dry. It was slowly decomposed by cold and rapidly by hot water, yielding, in addition to boric and acetic acids, 2-acetylanthragallolanthranol (m. p. 239—240°, decomp.) [Found by Dimroth's method (*loc. cit.*): 2-acetylanthragallolanthranol, 68.6, 69.8; acetic acid, 27.1, 26.4; boric acid, 13.7, 14.3.  $C_{16}H_{11}O_5B(OAc)_2$  requires 2-acetylanthragallolanthranol, 68.9; acetic acid, 29.1; boric acid, 15.05%].

We are much indebted to the British Alizarine Co. Ltd. for gifts of commercial 1-hydroxyanthraquinone, chrysazin and alizarin,

and to the British Dyestuffs Corporation Ltd. for anthragallol and for the preparation in considerable amount of alizarin 2-methyl ether.

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## XLV.—*The Development of Colour by Photochemical Change in Concentrated Solutions of Ammonium Thiocyanate.*

By B. S. SHARMA.

LIESEGANG (Eder's *Jahrb. Photographie*, 1894, 49) showed that the colour developed when concentrated aqueous solutions of ammonium thiocyanate are exposed to light is not due to traces of iron, and Holmes (J., 1926, 1690) attributed it to colloidal sulphur produced in the irreversible change  $\text{NH}_4\text{SCN} \rightarrow \text{NH}_4\text{CN} + \text{S}$ . Werner and Bailey (*ibid.*, p. 2970), however, dissented from this view and suggested that the cause might be found in some tautomeric form of thiocyanic acid or in the formation of a coloured complex between thiocyanic acid and the solvent. Bhatnagar and others (*J. Indian Chem. Soc.*, 1927, 4, 229) concluded that the colour was due to cyanogen sulphide and that the precipitate was a polymeride  $(\text{CNS})_x$ , suggesting the mechanism  $\text{NH}_4\text{CNS} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{HCNS}$ ,  $2\text{HCNS} + \text{O} \rightarrow \text{H}_2\text{O} + 2\text{CNS}$ ,  $x(\text{CNS}) \rightarrow (\text{CNS})_x$ . Montignie (*Bull. Soc. chim.*, 1928, 43, 106) and Patten and Smith (*Trans. Roy. Soc. Canada*, 1928, 22, III, 221) considered ferric thiocyanate to be responsible for the colour. According to Montignie, the reaction  $2\text{FeSO}_4 + \text{O} + 6\text{HCNS} \rightleftharpoons \text{H}_2\text{O} + 2\text{H}_2\text{SO}_4 + 2\text{Fe}(\text{CNS})_3$  occurs.

The work now described (finished before the last two papers were available) was initiated in view of the conflicting nature of the foregoing conclusions.

### EXPERIMENTAL.

1. Samples of ammonium thiocyanate which did not give rise to the colour on insolation were produced (i) by the action of either ammonium carbonate or ammonium sulphate on barium thiocyanate, prepared by treating ammonium thiocyanate with baryta, and also (ii) by boiling a fairly dilute solution of the salt with animal charcoal, boiled with pure hydrochloric acid and dried before use. Moreover, these samples did not develop colour when treated with pure hydrochloric acid, hydrogen peroxide, or chlorine.

2. Iron was detected in the salt by arc and spark spectral lines.



3. Traces of iron (as ferrous or ferric salt or as metal) added to the pure samples produced a colour upon insolation.

4. Both the intensity of the colour developed and the time required for its disappearance in the dark were proportional to the amount of iron introduced.

5. The ethereal extract of the colour developed with ferrous salt and ammonium thiocyanate was intensified by dilution.

6. A solution in water-free pyridine exhibited a photochemical change similar to that in aqueous solution.

7. Even after repeated insolutions and storage in the dark, aqueous solutions yielded no precipitate.

8. Gelatin inhibited the development of the colour.

*Discussion.*—Expts. 1, 2, and 3 show that traces of iron present as impurity are responsible for the coloration. Expt. 4 rules out the possibility that the iron functions as a catalyst, and shows that it actually takes part in the formation of the coloured compound, light supplying the energy. The formation of ferric thiocyanate is doubtful, for it is decolorised neither by heating (Scott, "Standard Methods of Analysis," 4th edtn., 1927, 246) nor by keeping in the dark (Dhar, *J. Indian Chem. Soc.*, 1929, 6, 143); moreover, it is bleached by light, and is entirely extracted by ether, the extract leaving a coloured residue on evaporation, whereas the extract from the insolated solutions does not behave so. The photochemical colour, produced with traces of ferric iron insufficient to show coloration ordinarily, can hardly be due to ferric thiocyanate (compare *J. Soc. Chem. Ind.*, 1929, 48, 336t). Expt. 5 distinguishes the colour developed with ferrous iron from that of ferric thiocyanate. Expt. 6 shows that the colour is probably not dependent upon hydrolysis or upon oxygen-containing solvents. The photochemical change in Expt. 7 appears to be reversible. The ready disappearance of the colour in the dark, on heating, or on dilution, its non-appearance in the absence of oxygen and traces of iron, and its appearance at high concentrations show that the compound is a sort of loose additive complex of ferrous thiocyanate with oxygen, and that its formation is probably connected with the changes at high concentrations.

Further work on the subject is in progress.

The author's thanks are due to Dr. H. B. Dunncliff for his interest in the work, and to Pundit M. M. Malinya, the Vice-Chancellor of the Benares University, for affording laboratory facilities.

GOVERNMENT COLLEGE, LAHORE,  
AND BENARES UNIVERSITY.

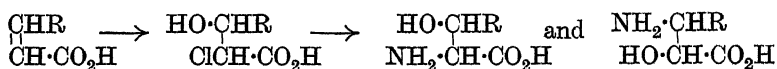
[Received, September 9th, 1929.]

XLVI.—*Hydroxyamino-acids.*

By WILLIAM JOHN NOBBS BURCH.

DAKIN has shown (*J. Biol. Chem.*, 1921, 48, 273) that maleic acid on treatment with chlorine water gives chlorohydroxysuccinic acid, which is converted by the action of ammonia into hydroxyaspartic acid.

Acrylic, crotonic, and tiglic acids behave in the same way under such conditions, giving mixtures of the  $\alpha$ - and  $\beta$ -acids :



Glutaconic acid, however, behaves abnormally, giving *dihydroxyglutaramic acid*, possibly owing to the intermediate formation of a lactam,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CO}$ . The conversion of chloro-

hydroxyglutaric acid into hydroxyglutamic acid by Gabriel's phthalimide process has been unsuccessfully attempted.

## EXPERIMENTAL.

*Preparation of Glutaconic Acid.*—Ethyl sodio- $\alpha,\gamma$ -dicarbethoxyglutaconate (Ingold and Perren, *J.*, 1921, 119, 1591) was converted into glutaconic acid by a method communicated to the author by Dr. G. A. R. Kon. The tetracarboxylic ester was liberated from the sodium derivative by means of a mineral acid in the presence of ether and, without being dried, the ethereal solution was evaporated. The ester was then heated with alcohol ( $\frac{1}{2}$  vol.) and 10% hydrochloric acid (3 vols.) until all the oil disappeared and no oil separated on cooling (5 hours). The alcohol was distilled off, and glutaconic acid (m. p. 132°) crystallised on cooling; a little more was obtained by extracting the mother-liquor with ether, drying the extract with sodium sulphate, concentrating it and adding benzene.

*Barium  $\alpha$ -Chloro- $\beta$ -hydroxyglutarate.*—Glutaconic acid (10 g.) was treated with a large excess of hypochlorous acid (prepared by extracting bleaching powder with water and distilling the extract in a vacuum with the calculated quantity of 5% nitric acid), after 24 hours the mixture was exactly neutralised with baryta and the filtered solution was concentrated in a vacuum, finally over concentrated sulphuric acid; the yellow crystals obtained (16 g.; yield, 66%) were recrystallised from water (Found: Ba, 43.5; Cl, 11.0.  $\text{C}_5\text{H}_4\text{O}_5\text{ClBa}$  requires Ba, 43.2; Cl, 11.2%).

*Ammonium Dihydroxyglutaramate*.—Barium  $\alpha$ -chloro- $\beta$ -hydroxyglutaramate was converted into *ammonium dihydroxyglutaramate* by removing the barium as sulphate and adding methyl alcohol saturated with ammonia.

A better yield was obtained as follows: A mixture of 10 g. of glutamic acid with a large excess of hypochlorous acid was kept for 24 hours and then evaporated to small bulk in a vacuum at 50°. Methyl alcohol saturated with dry ammonia was added in excess, and the mixture left in a stoppered bottle. Rosettes of tiny platelets began to form after 24 hours and the reaction was complete in about a week. The crystals were recrystallised from aqueous alcohol (yield, 6 g. or 43% of the theoretical) [Found: total N (by Kjeldahl's method), 15.65; N (as  $\text{NH}_4$ ), 7.0; C, 34.3; H, 6.7.  $\text{C}_5\text{H}_{12}\text{O}_5\text{N}_2$  requires total N, 15.55; N (as  $\text{NH}_4$ ), 7.8; C, 34.1; H, 6.8%].

*Dihydroxyglutaramic Acid*,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}_2$ .—The ammonium salt was treated in aqueous solution with silver oxide, and the product with hydrogen sulphide. The crystalline material obtained did not give the ninhydrin reaction for  $\alpha$ -amino-acids, and in an estimation of amino-nitrogen by Van Slyke's method, no nitrogen was obtained after 24 hours by means of acetic acid; the theoretical amount was evolved, however, after 24 hours on treatment with sodium nitrite and concentrated hydrochloric acid (Plimmer, J., 1925, 127, 2651). On prolonged boiling with baryta, the whole of the nitrogen in the compound was obtained as ammonia. The *acid* reduced ammoniacal silver nitrate and gave a deep blue colour with copper sulphate solution and caustic soda [Found: total N (by Kjeldahl's method), 8.4; N (by Van Slyke's method as above), 8.5; C, 36.5; H, 5.6; *M* (by means of the silver salt), 163.  $\text{C}_5\text{H}_9\text{O}_5\text{N}$  requires N, 8.6; C, 36.8; H, 5.5%; *M*, 163].

*$\alpha$ -Amino- $\beta$ -hydroxybutyric Acid*.—A solution of 4.5 g. of crotonic acid in water was mixed with hypochlorous acid (25% excess) and, after 12 hours, evaporated under diminished pressure. A solution of the residual yellow syrup in methyl alcohol was cooled in ice, saturated with dry ammonia, and heated in an autoclave at 120° for 10 hours. On cooling, no crystals formed. The solution was treated with an excess of baryta, the ammonia removed by aeration and the barium with sulphuric acid, the filtrate boiled with lead oxide to remove chloride, and the lead removed with hydrogen sulphide. The filtrate was treated with silver oxide to ensure complete removal of sulphide and chlorine, filtered, and evaporated in the dark; *silver  $\alpha$ -amino- $\beta$ -hydroxybutyrate* crystallised in thin platelets, which rapidly darkened in light (Found: Ag, 47.2.  $\text{C}_4\text{H}_8\text{O}_3\text{NAg}$  requires Ag, 47.8%).

The acid was obtained by removing the silver with hydrogen

sulphide, and the hydrogen sulphide by aeration. On evaporation in a vacuum, a pale yellow syrup was obtained which slowly crystallised in a vacuum over concentrated sulphuric acid (yield, 2.7 g.; 45% of the theoretical) [Found: total N (Kjeldahl), 11.6; amino-N (Van Slyke), 11.3. Calc. for  $C_4H_9O_3N$ : N, 11.8%]. The acid is very deliquescent, gives a strong ninhydrin reaction, and forms a pale blue crystalline copper salt and well-defined crystalline salts with cinchonine and quinine (Found for the *cinchonine* salt: N, 10.0.  $C_4H_9O_3N \cdot C_{19}H_{22}ON_2$  requires N, 10.2%).

The positive ninhydrin reaction and the fact that the total amino-nitrogen is only obtained after 10 minutes' shaking with sodium nitrite and glacial acetic acid suggest that the product of the above reaction is a mixture of the  $\alpha$ - and  $\beta$ -amino-acids.

*$\alpha$ -Amino- $\beta$ -hydroxy- $\alpha$ -methylbutyric Acid,*



—Tiglic acid (5 g.) was treated in the same way as the crotonic acid in the previous experiment. The *silver* salt is a white powder (Found: Ag, 44.6.  $C_5H_{10}O_3NAg$  requires Ag, 45.0%). The *acid* was obtained as a yellow syrup which slowly crystallised [Found: N (Kjeldahl), 10.3; amino-N (Van Slyke), 10.1.  $C_5H_{11}O_3N$  requires N, 10.5%]. All the preceding statements regarding  $\alpha$ -amino- $\beta$ -hydroxybutyric acid apply also to this acid (Found for the *brucine* salt: N, 7.5.  $C_5H_{11}O_3N \cdot C_{23}H_{28}O_4N_2$  requires N, 8.0%).

*isoSerine*.—This was similarly prepared from acrylic acid (Melikow, *Ber.*, 1880, 13, 1265). It gave the ninhydrin reaction, and the total amino-nitrogen was evolved only after 10 minutes' shaking with glacial acetic acid and sodium nitrite: this suggests that this product also is a mixture of serine and isoserine (the  $\alpha$ - and  $\beta$ -amino-acids).

*Hydroxyaspartic Acid*.—Maleic acid was converted in the same way and also by Dakin's method (*loc. cit.*) into hydroxyaspartic acid. The compound obtained by either method gave the ninhydrin reaction, and the whole of the amino-nitrogen was evolved after 5 minutes' shaking with glacial acetic acid and sodium nitrite.

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[Received, December 2nd, 1929.]

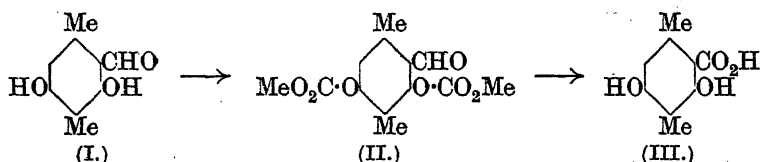
XLVII.—*Lichen Acids. Part I. Derivatives of  $\beta$ -Orcinol.*By ALEXANDER ROBERTSON and RICHARD  
JOHN STEPHENSON.

ALTHOUGH  $\beta$ -orcinol, the homologue of orcinol, was isolated in 1848 by Stenhouse (*Annalen*, **68**, 104) as a product of the action of lime-water on impure usnic acid from *Usnea ceratina*, it was not until 1880 that Stenhouse and Groves (*J.*, **37**, 405) were able to show that the phenol was derived from barbatic acid, which they obtained from *U. barbata*. This acid has since been isolated from a number of lichens, in which it invariably occurs along with usnic acid (for references, see Perkin and Everest, "Natural Organic Colouring Matters," 1918, pp. 530—542). Hesse (*Ber.*, 1898, **31**, 664; *J. pr. Chem.*, 1898, **58**, 526; 1903, **68**, 14) found that barbatic acid on hydrolysis gave rhizonic acid in addition to  $\beta$ -orcinol; rhizonic acid he believed to be the monomethyl ether of  $\beta$ -orcinolcarboxylic acid, and the depside to be derived from  $\beta$ -orcinolcarboxylic acid and rhizonic acid. The  $\beta$ -orcinol nucleus has since been found to occur in a number of depsides—atranorin (Hesse, *Ber.*, 1897, **30**, 358; *J. pr. Chem.*, 1898, **57**, 280), dirhizonic acid (Hesse, *ibid.*, 1898, **58**, 531; 1906, **73**, 120), soloric acid (Zopf, *Annalen*, 1909, **364**, 307; Hesse, *J. pr. Chem.*, 1915, **92**, 425), and armoric acid (Hesse, *ibid.*, 1907, **76**, 7).

In a study of the constitution of these depsides by synthetical means, it was essential first to devise a method for the preparation of  $\beta$ -orcinol in quantity, Kostanecki's process (*Ber.*, 1886, **19**, 2323) having been found unsuitable. Reduction of 2:6-dinitro-*p*-xylene (prepared from *p*-xylidine by Sonn's method; *Ber.*, 1916, **49**, 621) by ammonia and hydrogen sulphide invariably gave poor yields of 6-nitro-*p*-2-xylidine, but reduction by sodium disulphide in aqueous-acetone solution proved effective. The nitroxylidine was converted into 6-nitro-*p*-2-xylenol (compare D.R.-PP. 95,359 and 97,012), the reduction of which to 6-amino-*p*-2-xylenol was conveniently effected in alcoholic solution by iron (compare West, *J.*, 1925, **127**, 494). Attempts to prepare  $\beta$ -orcinolcarboxylic acid by the method adopted by one of us (A. R.) and Robinson (*J.*, 1927, 2196) for the preparation of *p*-orsellinic acid failed (compare Kostanecki, *loc. cit.*).

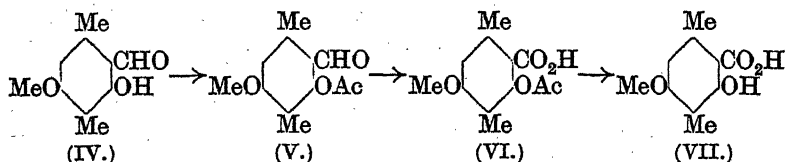
$\beta$ -Orcylaldehyde (I) was prepared by Gattermann's method (compare St. Pfau, *Helv. Chim. Acta*, 1928, **11**, 864): the dicarbo-methoxy-derivative (II) on oxidation with potassium permanganate

in acetone solution and hydrolysis of the product, gave  $\beta$ -orcinol-carboxylic acid (III).



The synthetic acid is identical with a specimen obtained by hydrolysis of the methyl ester prepared from atranorin by St. Pfau's method (*Helv. Chim. Acta*, 1926, 9, 650): the instability of the acid and its salts in warm aqueous solution may account for the inability of previous workers to isolate it by hydrolysis of the ester or of barbitic acid. The silver salt rapidly decomposed on exposure to light and was unsuitable for the preparation of esters. These, however, were readily formed in warm alcoholic solutions of the acid. The methyl ester thus obtained was identical with a specimen from atranorin. This ester has also been isolated from oak moss oil by Rosenthal and Walbaum (*Ber.*, 1924, 57, 770). Its reaction with ferric chloride depends on the concentration of the alcoholic solution—a fact which may account for the divergent results recorded by previous authors.

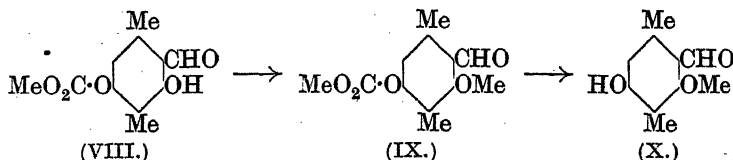
Partial methylation of  $\beta$ -orcyraldehyde (I) by the methyl iodide-acetone method (Robertson and Robinson, J., 1928, 1455) proved convenient for the preparation of rhizonaldehyde (IV). Sonn (*Ber.*, 1916, 49, 2589), who prepared this aldehyde from  $\beta$ -orcinol mono-methyl ether by the Gattermann method, believed it to be represented by the constitution (X) (*isorhizonaldehyde*).



The orientation of the ether (IV) determined by St. Pfau (*Helv. Chim. Acta*, 1928, 11, 864) has been confirmed, the condensation of (IV) with  $\omega$ -methoxyacetoveratrone giving 3:7:3':4'-tetramethoxy-5:8-dimethylflavylium chloride. Oxidation of the acetyl derivative (V) gave acetyl rhizonic acid (VI), which on deacetylation yielded rhizonic acid (VII). This acid (VII) has the properties attributed to it by St. Pfau (compare Sonn, *loc. cit.*).

Attempts to methylate the carbomethoxy-derivative (VIII) with diazomethane in ethereal solution failed, and when a mixture of nitrobenzene and ether was used a resinous product was obtained.

Agitation of an acetone solution of (VIII) containing methyl iodide and active silver oxide gave only a trace of (IX), but this was obtained when a methyl iodide solution of (VIII) was refluxed in presence of silver oxide. On hydrolysis, it gave *isorhizonaldehyde* (X) identical with that prepared by St. Pfau from  $\beta$ -orcinol mono-



methyl ether. As might be expected, the aldehyde (X) did not condense with  $\omega$ -methoxyacetovertone to give a flavylum salt. The production of (X) from (VIII) determines the orientation of the latter substance.

Experiments on the synthesis of barbatic acid and its ethyl ester are in progress.

#### EXPERIMENTAL.

**6-Nitro-p-2-xylylidine.**—A solution of sodium disulphide, prepared by refluxing a mixture of sulphur (16.5 g.), hydrated sodium sulphide (120 g.), and water (400 c.c.), was added in four portions to 2 : 6-dinitro-p-xylene (100 g.), dissolved in acetone (600 c.c.). When the vigorous reaction had ceased, the mixture was refluxed for 3 hours and poured into water (2 l.). After 12 hours, the solid was extracted three times with warm 10% hydrochloric acid, and on addition of aqueous ammonia to the combined extracts (1.5 l.) the nitroamine (68 g.) was obtained as a yellow solid, which crystallised from ligroin in orange-yellow needles, m. p. 96°.

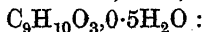
**6-Nitro-p-2-xylenol.**—A solution of the nitroamine (50 g.) in a mixture of concentrated sulphuric acid (100 c.c.) and water (200 c.c.) was poured on ice (300 g.) to ensure the separation of the sulphate in small crystals. Sodium nitrite (20.7 g.), dissolved in water (100 c.c.), was then introduced, and the mixture stirred for 1.5 hours. The filtered diazo-solution was gradually added to boiling 30% sulphuric acid (300 c.c.); on cooling, the nitroxylenol separated. Crystallisation from water and then from ligroin gave the product (37 g.) in orange-yellow plates, m. p. 91°. The crude nitroxylenol, which could not be employed for the next stage, can be purified by distillation under diminished pressure, b. p. 185–187°/20 mm.; the warm residue in the flask is, however, liable to explode.

**6-Amino-p-2-xylenol.**—A mixture of the nitroxylenol (50 g.), iron powder (50 g.), alcohol (300 c.c.), and concentrated hydrochloric acid (5 c.c.) was refluxed for 6 hours, a test then showing that the reduction was complete. The filtered solution was con-

centrated to 75 c.c., saturated with hydrogen chloride, and kept at 0° for some hours. The hydrochloride was collected and washed with 96% alcohol saturated with hydrogen chloride. The salt crystallised in colourless elongated prisms (38 g.). Saturated sodium bicarbonate solution liberated 6-amino-p-2-xylénol, which crystallised from water in fern-like clusters of colourless plates, m. p. 155° (Found: C, 70.1; H, 8.3.  $C_8H_{11}ON$  requires C, 70.0; H, 8.1%). The amine is readily soluble in alcohol and in acetone.

2 : 6-Dihydroxy-p-xylene ( $\beta$ -Orcinol).—The aminoxylénol hydrochloride (20 g.) was dissolved below 0° in a mixture of concentrated sulphuric acid (55 c.c.) and ice and water (800 c.c.). Sodium nitrite (8 g.), dissolved in water (100 c.c.), was then introduced, and the mixture stirred for 45 minutes. The diazonium salt solution was heated on the steam-bath until the evolution of nitrogen had almost ceased and was then boiled for 5 minutes. A little charcoal was added and the solution was filtered, cooled, and saturated with ammonium sulphate. Part of the  $\beta$ -orcinol crystallised; the remainder was isolated by three extractions with ether. The product (12 g.) crystallised from benzene in pink stellate aggregates of prisms, m. p. 163°; distillation gave a colourless specimen, b. p. 277—280°.

$\beta$ -Orcylaldehyde (I).—A mixture of  $\beta$ -orcinol (20 g.), anhydrous hydrogen cyanide (15 c.c.), and ether (300 c.c.) was saturated with hydrogen chloride. The aldimine hydrochloride, which separated in almost colourless prisms in 2 hours, was collected after 12 hours, washed with ether, and dissolved in cold water (400 c.c.). The solution was heated on the steam-bath for 2 hours; a part of the aldehyde crystallised and the remainder separated on cooling. Recrystallisation from 30% alcohol gave a hydrate (22 g.) in colourless needles, m. p. 168° (Found: C, 61.9; H, 6.5. Calc. for



C, 61.7; H, 6.3%. Found in a specimen dried at 105—110° for 6 hours: C, 65.1; H, 6.1. Calc. for  $C_9H_{10}O_3$ : C, 65.1; H, 6.0%) (St. Pfau, *loc. cit.*, gives m. p. 163—164°). The ferric chloride reaction in alcohol is reddish-violet and addition of the aldehyde to aqueous calcium hypochlorite gives an intense yellow coloration. Acetylation with acetic anhydride and potassium carbonate gave a product which could not be purified.

2 : 4-Dimethylcarbonato-3 : 6-dimethylbenzaldehyde (II).—8% Aqueous sodium hydroxide (62.5 c.c.) was gradually added with vigorous agitation to a solution of  $\beta$ -orcyaldehyde (8.8 g.) in a mixture of acetone (80 c.c.) and methyl chloroformate (14.5 g.). After  $\frac{1}{2}$  hour, saturated sodium bicarbonate solution (50 c.c.) was introduced and on dilution with water (300 c.c.) the dicarbomethoxy-



derivative separated as an oil which solidified on being scratched. The substance crystallised from ligroin in tufts of colourless slender needles (13 g.), m. p.  $91^{\circ}$  (Found: C, 55.4; H, 5.2.  $C_{13}H_{14}O_7$  requires C, 55.3; H, 5.0%). This carbonate is readily soluble in acetone and moderately readily soluble in cold alcohols. It does not give a ferric chloride reaction.

*2 : 4-Dihydroxy-3 : 6-dimethylbenzoic Acid* ( $\beta$ -Orcinolcarboxylic Acid) (III).—(A) Potassium permanganate (5 g.), dissolved in water (80 c.c.), was gradually added to a solution of 2 : 4-dimethylcarbonato-3 : 6-dimethylbenzaldehyde (3 g.) in acetone (50 c.c.) maintained at  $50$ – $55^{\circ}$ . After 15 minutes, the reaction mixture, cooled to  $0^{\circ}$ , was cleared with sulphur dioxide, and on slow evaporation of the acetone a colourless solid separated. A solution of the solid, collected after 3 days, in 4% aqueous sodium hydroxide (15 c.c.) was kept at room temperature for  $\frac{1}{2}$  hour, then cooled to  $0^{\circ}$ , and acidified with 10% hydrochloric acid (10 c.c.). The precipitate was dissolved in saturated aqueous sodium bicarbonate (75 c.c.), and the solution filtered from traces of  $\beta$ -orcylaldehyde. Acidification with 10% hydrochloric acid gave almost pure  $\beta$ -orcinolcarboxylic acid (1 g.). Warm water was added to a solution of the substance in warm acetone until a faint turbidity appeared; the cooled solution gave the acid in elongated silky needles, m. p.  $184^{\circ}$  (decomp. to  $\beta$ -orcinol and carbon dioxide) (Found: C, 59.3; H, 5.7.  $C_9H_{10}O_4$  requires C, 59.4; H, 5.5%). The acid is readily soluble in alcohol and in acetone and sparingly soluble in cold water. It decomposes in boiling water to  $\beta$ -orcinol and carbon dioxide. The ferric chloride reaction in alcoholic solution is intense bluish-violet. Addition of the acid to aqueous calcium hypochlorite solution gives a transient blood-red coloration.

A solution of the acid (0.8 g.) in absolute methyl alcohol (20 c.c.) was refluxed for 4 hours, and the methyl ester precipitated from the cooled solution by means of 1% aqueous sodium bicarbonate (50 c.c.). The ester crystallised from 50% methyl alcohol in colourless, elongated, slender prisms, m. p.  $143^{\circ}$  alone or mixed with a natural specimen prepared from atranorin (Found: C, 61.1; H, 6.1. Calc. for  $C_{10}H_{12}O_4$ : C, 61.2; H, 6.2%). Ferric chloride added to a dilute alcoholic solution gives a greenish-brown coloration, which becomes brownish-purple on addition of water. A concentrated alcoholic solution gives a brownish-purple colour, unchanged by dilution with alcohol or by addition of water. The calcium hypochlorite coloration is a transient orange.

The *ethyl* ester was isolated from a solution of the acid (0.8 g.) in absolute alcohol (20 c.c.) which had been maintained at  $75^{\circ}$  for 6 hours. Crystallisation from 50% alcohol gave colourless slender

needles, m. p. 129° (Found: C, 62.8; H, 6.9.  $C_{11}H_{14}O_4$  requires C, 62.8; H, 6.7%). The ferric chloride coloration is purple, and the calcium hypochlorite an intense orange which rapidly fades.

(B) A solution of methyl  $\beta$ -orcinoicarboxylate (from atranorin) 5 g.) in 10% aqueous potassium hydroxide solution was kept in a tightly stoppered vessel at room temperature for 50 hours. The reddish-brown solution, cooled to 0°, was acidified with 10% hydrochloric acid. After  $\frac{1}{2}$  hour, the cream-coloured precipitate was collected and extracted with cold saturated sodium bicarbonate solution (100 c.c.). Addition of 10% hydrochloric acid to the solution, filtered from traces of unchanged ester, gave the acid (III) (3 g.), which crystallised from acetone-water in elongated silky needles, m. p. 184° (decomp.) alone or mixed with a synthetic specimen (Found: C, 59.2; H, 5.7%). The colour reactions are identical with those given by the synthetic acid.

2-Acetoxy-4-methoxy-3:6-dimethylbenzaldehyde (*Acetyl rhizonaldehyde*) (V).—A mixture of  $\beta$ -orcylaldehyde (10 g.), methyl iodide (8.2 g.), potassium carbonate (10 g.), and acetone (75 c.c.) was refluxed for 1½ hours; a further quantity of iodide (4.1 g.) was added after 45 minutes. After removal of the potassium salts and acidification with acetic acid, the mixture deposited rhizonaldehyde (IV) (7 g.); a further quantity (3 g.) was obtained by evaporation of the acetone residue, and by dissolving the potassium salts in 50% acetic acid. The substance crystallised from 50% alcohol in colourless prisms, m. p. 136° (Found: C, 66.6; H, 6.7. Calc. for  $C_{10}H_{12}O_3$ : C, 66.6; H, 6.7%). The ferric chloride reaction is reddish-brown. This aldehyde does not give a coloration with calcium hypochlorite.

Rhizonaldehyde (10 g.), on treatment with acetic anhydride (75 c.c.) and sodium acetate (10 g.) during 3 hours on the steam-bath, gave the *acetyl* derivative (V) (11 g.), which crystallised from 40% alcohol in colourless needles, m. p. 71° (Found: C, 64.9; H, 6.6.  $C_{12}H_{14}O_4$  requires C, 64.9; H, 6.3%). The substance is easily soluble in alcohol and acetone and does not give a ferric chloride reaction.

4% Aqueous sodium hydroxide solution (8 c.c.) was added to a mixture of rhizonaldehyde (1 g.), methyl chloroformate (1 g.), and acetone (25 c.c.) cooled to 0° (agitation). The carbomethoxy-derivative separated on addition of dilute sodium bicarbonate solution (40 c.c.) and was collected after 3 hours. It crystallised from light petroleum in clusters of prisms, m. p. 90°, which gave a faint brown ferric chloride coloration.

3:7:3':4'-Tetramethoxy-5:8-dimethylflavylum Ferrichloride.—Dark red needles with a green reflex separated when hydrogen chloride was passed into a solution of rhizonaldehyde (0.75 g.) and

$\omega$ -methoxyacetoveratrone (0.5 g.) in ethyl acetate (40 c.c.). After 3 days, the chloride was collected and converted into the *ferrichloride*, which crystallised from a mixture of formic and acetic acids (equal vols.) in dark red needles, m. p. 240—245° after sintering at 236° (Found: C, 45.6; H, 4.4.  $C_{21}H_{23}O_5Cl_4Fe$  requires C, 45.4; H, 4.2%).

*2-Acetoxy-4-methoxy-3:6-dimethylbenzoic Acid (Acetyl rhizonic Acid) (VI).*—Potassium permanganate (5 g.), dissolved in water (80 c.c.), was gradually added to a solution of acetyl rhizonaldehyde (4 g.) in acetone (50 c.c.) maintained at 50°. The solution, cooled to 0°, was cleared with sulphur dioxide, and on slow evaporation of the acetone *acetyl rhizonic acid*, mixed with a trace of unchanged aldehyde, crystallised. The acid (purified by solution in aqueous sodium bicarbonate as described for  $\beta$ -orcinolcarboxylic acid) crystallised from acetone–water (equal vols.) in rectangular plates, m. p. 146° (decomp.) (Found: C, 60.7; H, 5.8.  $C_{12}H_{14}O_5$  requires C, 60.5; H, 5.9%). It is readily soluble in acetone and alcohol and sparingly soluble in warm water, from which it separates in small plates.

A solution of the acetyl derivative (2 g.) in 4% aqueous sodium hydroxide solution was kept at room temperature for 3 hours. Acidification of the solution with dilute hydrochloric acid then gave rhizonic acid (VII), which crystallised from acetone–water in hexagonal plates, m. p. 232° (Found in a specimen dried at 100°: C, 61.1; H, 6.4. Calc. for  $C_{10}H_{12}O_4$ : C, 61.2; H, 6.2%). Addition of ferric chloride to an alcoholic solution gives a brown coloration, which becomes intense blue-violet on addition of water. The calcium hypochlorite coloration is yellow.

*2-Hydroxy-4-methylcarbonato-3:6-dimethylbenzaldehyde (VIII).*—4% Aqueous sodium hydroxide solution (25 c.c.) was gradually added to a mixture of  $\beta$ -orcyraldehyde (4 g.), acetone (40 c.c.), and methyl chloroformate (2.4 g.) cooled to 0° (agitation). After  $\frac{1}{2}$  hour, aqueous sodium bicarbonate (200 c.c.) was introduced, and after 2 hours the *carbomethoxy*-derivative was isolated; it crystallised from 70% acetone in masses of colourless slender needles, m. p. 110° (Found: C, 58.7; H, 5.6.  $C_{11}H_{12}O_5$  requires C, 58.9; H, 5.4%). The substance is easily soluble in acetone and in alcohol and insoluble in water. It crystallises from light petroleum in tiny prisms. The ferric chloride coloration is red-brown.

*2-Methoxy-4-methylcarbonato-3:6-dimethylbenzaldehyde (IX).*—Active silver oxide was added to a solution of the foregoing carbomethoxy-derivative (5 g.) in methyl iodide (30 c.c.), and the mixture refluxed until a sample did not give a ferric chloride reaction. The silver oxide was removed by filtration and washed with acetone

(150 c.c.). Evaporation of the combined filtrates gave a semi-solid product, which was extracted with boiling ligroin. The extract, decanted from the insoluble residue and cooled, gave the *ether* (IX) in tufts of colourless elongated prisms (4 g.), m. p. 74—75° (Found : C, 60.6; H, 6.2.  $C_{12}H_{14}O_5$  requires C, 60.5; H, 5.9%). The substance is readily soluble in alcohol and acetone and sparingly soluble in light petroleum.

A solution of the foregoing ether (0.6 g.) in 4% methyl-alcoholic sodium hydroxide (5 c.c.) was kept at room temperature for  $\frac{1}{2}$  hour, then acidified with 50% acetic acid, and diluted with water (40 c.c.); *isorhizonaldehyde* (X), thus precipitated, crystallised from 25% methyl alcohol in slender needles, m. p. 151°. This aldehyde does not give a ferric chloride reaction.

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[Received, December 5th, 1929.]

## NOTES.

*The Interaction of Sodamide and Alkyl Iodides with Acetophenone and its Homologues.* By ALFRED RUSSELL.

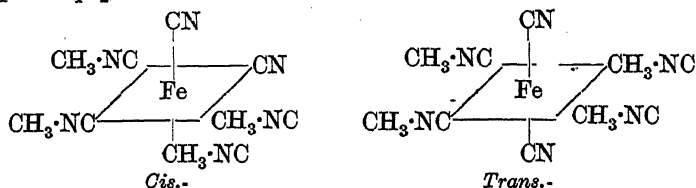
NORMAL reaction, producing more than 50% of the theoretical yield of  $\alpha$ -ethyl- $\alpha$ -*n*-propyl- $\alpha$ -*n*-butylacetophenone, occurs between ethyl iodide and sodio-*n*-propyl-*n*-butylacetophenone in a neutral solvent (compare Haller and Bauer, *Compt. rend.*, 1909, **148**, 70).

In ether, the reaction between sodioacetophenone and methyl iodide also is normal; but in benzene no propiophenone is formed, the sole product being a *polymeride*,  $(C_6H_5 \cdot CO \cdot C_2H_5)_3$ , a white amorphous solid, m. p. 96—98°, b. p. 300—320°/15 mm. [Found : C, 81.1; H, 7.3; *M*, mean of ten determinations, 405.  $(C_6H_5 \cdot CO \cdot C_2H_5)_3$  requires C, 80.6; H, 7.3%; *M*, 402]. The substance is unaffected by acids or alkalis, permanganate, dichromate, and fusion with caustic potash, chars when heated strongly in the air, and is readily soluble in the common organic solvents but insoluble in water, acids, or alkalis. It gives no methyl iodide in the Zeisel reaction and is therefore not a trimethoxytriphenylcyclohexane. It may have a structure,  $O \begin{array}{c} \text{C} \text{Et} \text{Ph} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{C} \text{Et} \text{Ph} \cdot \text{O} \end{array}$ , similar to that of the acetals, which it resembles in chemical stability.—THE SIR DONALD CURRIE LABORATORIES, THE QUEEN'S UNIVERSITY, BELFAST. [Received, October 25th, 1929.]

*The Structure of the Isomeric Methyl Ferrocyanides.*

By S. GLASSTONE.

ALTHOUGH the suggestion that potassium ferrocyanide exists in two isomeric forms (Briggs, J., 1911, **99**, 1019) has been shown to be erroneous (Bennett, J., 1917, **111**, 490; Kolthoff, *Chem. Weekblad*, 1919, **16**, 1406; Briggs, J., 1920, **117**, 1026), the isomerism of the tetramethyl ferrocyanides (Hartley, J., 1913, **103**, 1196) appears to be well established. Hitherto, however, there has been no satisfactory explanation of this isomerism, and the following view is therefore proposed. If the structure of the so-called methyl ferrocyanide is considered to be  $[\text{Fe}(\text{CH}_3\cdot\text{NC})_4(\text{CN})_2]$ , with the four neutral  $\text{CH}_3\cdot\text{NC}$  groups (compare Hartley, J., 1911, **99**, 1549) co-ordinated to the iron atom (see Pfeiffer, "Organische Molekülverbindungen," 1927, p. 193, for other instances), the two valency electrons of the latter are shared with the two cyanide radicals, and the substance will be a non-electrolyte. Further, since it is of the type  $\text{MX}_4\text{A}_2$ , it can exist in *cis*- and *trans*-modifications, thus :



The *cis*-form, having adjacent polar cyanide radicals, is presumably the more soluble and more reactive; hence it corresponds to Hartley's  $\alpha$ -form. The substance  $(\text{CH}_3)_6\text{Fe}(\text{NC})_6\text{I}_2$ , produced by the action of methyl iodide on the  $\alpha$ -form, is probably  $[\text{Fe}(\text{CH}_3\cdot\text{NC})_6]\text{I}_2$  [compare  $\text{Mg}(\text{CH}_3\cdot\text{CN})_6\text{I}_2$ , possibly  $\text{Mg}(\text{CH}_3\cdot\text{NC})_6\text{I}_2$ ; Menschutkin, *Z. anorg. Chem.*, 1909, **61**, 110] and should be an electrolyte. The chloride and sulphate prepared by Hartley (J., 1910, **97**, 1725) are probably analogous.—THE UNIVERSITY, SHEFFIELD. [Received, November 21st, 1929.]

# XLVIII.—*The Catalytic Hydrogenation of Different Types of Unsaturated Compounds. Part V. The Hydrogenation of Cyclic Ethylenic Derivatives and of their Mixtures.*

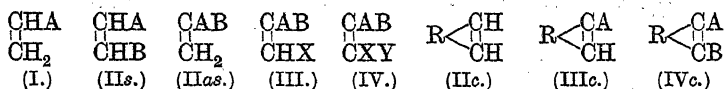
By SERGUEY V. LEBEDEV and MICHAÏL PLATONOV.

THE following communication is closely connected with Part I of our investigation (J., 1925, **127**, 417), in which it was shown that the rate and nature of hydrogenation of single ethylenic compounds

and of their mixtures are determined by the characteristics of the type to which they belong (i.e., by the degree of substitution at the double linkage in the molecule) rather than by individual characteristics. Thus, in every case, monosubstituted ethylenic derivatives are hydrogenated preferentially, and tetrasubstituted last of all, the di- and tri-substituted types being intermediate.

This property is most marked in the hydrogenation of mixtures of different ethylenic derivatives. Compounds of the same degree of substitution at the double bond are hydrogenated concurrently in a mixture and their curves show no break, but those of different types are hydrogenated consecutively in the above order, so that their curves display definite breaks corresponding roughly to the end of hydrogenation of one component and the beginning of that of another. This is probably due to the fact that the affinity of the catalyst for monosubstituted is much greater than for poly-substituted ethylenic compounds, those of the same degree of substitution being adsorbed with approximately equal readiness.

Discussion is simplified by the following classification of ethylenic compounds according to the degree of substitution at the double bond, *c* denoting a cyclic structure and *R* the remainder of the ring system.



The present communication deals primarily with ethylenic derivatives in a *cyclohexane* ring, other cyclic systems being reserved for a future paper. We have studied the hydrogenation of single representatives of this class, and of their mixtures with one another and with open-chain ethylenic derivatives (in all, about forty binary mixtures were examined) and the results conform to the general rules given above for open-chain compounds. In those cases in which the hydrogenation of a mixture of two compounds shows a break in the curve, we are justified in assuming that both components are often (or perhaps always) hydrogenated simultaneously in each section, and this conclusion is supported by an examination of the distribution of hydrogen between the components in different phases of the process.

We have found that in some binary mixtures *practically* pure components are hydrogenated on both sections, whereas in other cases there are mixtures capable of being analytically separated.

We have also found that the position of the break on the curves of practically all of the binary mixtures examined of an open-chain (see Part I) and a cyclic ethylenic derivative exactly corresponds with the

consecutive hydrogenation of the pure components in the mixture. As appreciable deviations from this rule are extremely rare, it is possible to calculate the composition of the mixture to within a few units % from the volume of hydrogen absorbed on the different portions of the curve.

Two such deviations are shown in Fig. 8 (curves 1 and 4), the breaks being considerably removed from the calculated positions in each case. The only other deviation is much more peculiar. It was noted in the pair carvone-camphene (Fig. 11, Curve 3); here we have a mixture of two types of substitution at the double bond, *viz.*, an *as.*-disubstituted ethylene (in both camphene and carvone) and a trisubstituted one (in carvone), yet we find on the hydrogenation curve three sharply separated sections instead of the two expected. This case requires further study.

#### EXPERIMENTAL.

The method of investigation was the same as described in Part I. 0.02—0.0025 G.-mol. of the substance was used, and, unless otherwise stated, the other conditions were: 0.2 g. of platinum-black, 15—25 c.c. of alcohol as solvent, and a bath temperature of 20°. The curves are plotted as before, the transverse dash in each case indicating the point at which the preferentially hydrogenated compound is calculated to be saturated. Since *rate* of absorption is plotted against time, the volume of hydrogen absorbed up to any given time is given by the *area* under the curve.

#### *Hydrogenation of Single Compounds* (Table I).

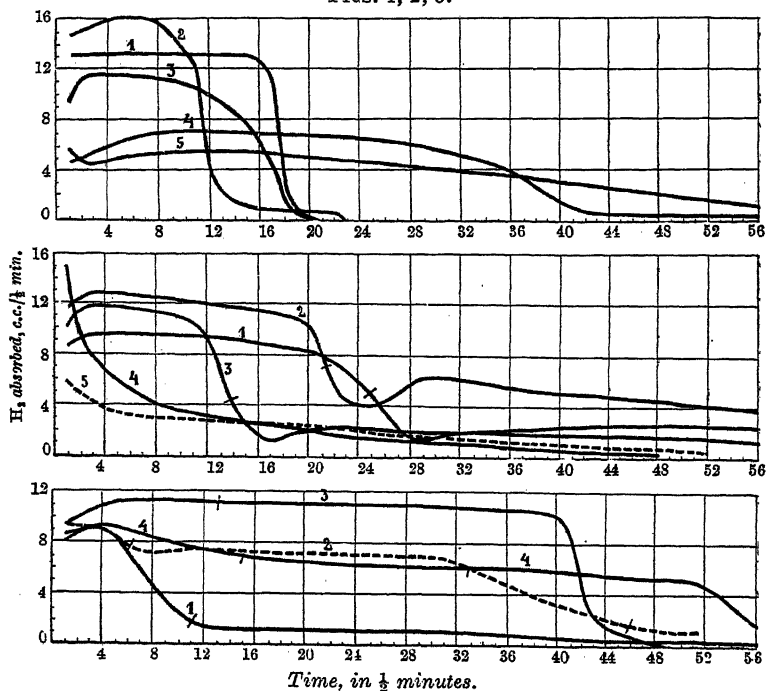
*Disubstituted Compounds* (Type IIc; Fig. 1).—The curves for cyclohexene (Curve 1) and 1-methyl- $\Delta^3$ -cyclohexene (Curve 2) are very much alike; the rate is nearly constant to the end, and the reaction ceases sharply with the absorption of 100% of the hydrogen calculated for saturation of the latter and of about 90% of that calculated for the former.\* The rate of hydrogenation of indene (Curve 3) is lower, and the curve droops slightly. A fourth compound of this type examined was maleic anhydride (obtained by the method of Tanatar, *J. Russ. Phys. Chem. Soc.*, 1890, 22, 213; m. p. 52—55.5°). Its hydrogenation gave an entirely unexpected result; for the absorption in ethereal solution was exceedingly low. Several experiments showed that the hydrogenation of cyclohexene is hindered by the presence of this anhydride; and hence we conclude that maleic anhydride is an anti-catalyst, although neither the acid itself nor its esters possess this quality. Citraconic acid

\* The cyclohexene contained about 10% of benzene or some other hydrocarbon very little susceptible to hydrogenation.

and its anhydride (Type IIIc) behave similarly. An investigation of this phenomenon in anhydrides and acids is being undertaken.

*Trisubstituted Compounds* (Type IIIc; Figs. 1 and 2).—Menthene and pinene are hydrogenated very slowly, their curves falling continuously. Both seem to contain a proportion of some compound (? dipentene) having a higher absorption rate, as shown by the initial rapid fall (Fig. 2, Curves 4 and 5).

FIGS. 1, 2, 3.



The curves of terpineol and carvotanacetone are very much alike (Fig. 1, Curves 5 and 4): the rate of absorption rises somewhat at first, and then falls continuously to the end. The latter compound was prepared by 50% hydrogenation of carvone in the absence of solvent (compare Armstrong, *Chem. and Ind.*, 1925, 44, 701), and since its oxime (m. p. 74–76°) and semicarbazone (m. p. 171–172.5°) showed it to be pure, we are convinced that in the hydrogenation of carvone the double bond in the side-chain (Type IIas) is reduced before that in the ring system (Type IIIc).

The absorption curves of carvone and *l*-limonene resemble one another (Fig. 2, Curves 1 and 2): in both cases hydrogenation of the bond in the side chain proceeds first and at an almost constant



TABLE I.

Compound.	Fig. and curve Nos.	Amount, g.	Temp. and press. of H <sub>2</sub> .	H <sub>2</sub> absorbed, c.c.	
				Calc.	Found.
<i>cyclo</i> Hexene	1; 1	0.8700	19°; 745 mm.	259	239.5†
1-Methyl- $\Delta^3$ - <i>cyclo</i> -hexene	1; 2	0.747	17° 768	183	179.3
Indene*	1; 3	0.8200	17° 744	171.5	175
Carvotanacetone	1; 4	1.5409	17° 758	241	229
Terpineol	1; 5	1.367	16° 758	211	228
Menthene*	2; 4	0.763	16° 757	124	141.5
Pinene*	2; 5	0.6493	17° 757	113	122
Carvone*	2; 1	1.394	18° 755	435	438
<i>l</i> -Limonene	2; 2	1.3800	18° 765	481.5	491
	2; 3	0.8500	14° 768	291	287
1 : 2-Dimethyl- $\Delta^1$ - <i>cyclo</i> hexene	3; 1	0.718	16°; 758	155	118†
		3.065	17°; 765	659	—†

\* Bath temperature, 15°.

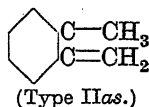
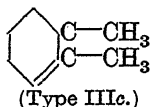
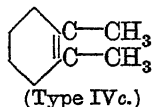
† Hydrogenation incomplete.

‡ See footnote, p. 323.

rate. The end of the absorption of the first molecule of hydrogen is marked by a sharp break in the velocity of reaction (compare Vavon, *Compt. rend.*, 1911, 152, 1675), which falls to a minimum and then increases somewhat. The second portions of the curves are like those of carvotanacetone and terpineol, in that the rate rises slightly at first and then falls slowly till the end of the reaction. In the case of carvone, after the absorption of 2 mols. of hydrogen a very slow hydrogenation of the ketonic group sets in. A second experiment with *l*-limonene (Fig. 2; Curve 3) was carried out with platinum-black which had been used previously; the rate of hydrogenation of the cyclic bond (Type IIIc) was somewhat slower, but that of the side-chain bond (Type IIas) remained practically the same.

*Tetrasubstituted Compounds* (Type IVc; Fig. 3).—Only one compound of this type was available, *viz.*, 1 : 2-dimethyl- $\Delta^1$ -*cyclo*-hexene, prepared as follows: 2-methyl*cyclo*hexanol was oxidised to the ketone by Sabatier's method (*Compt. rend.*, 1905, 141, 20), and this was treated with magnesium methyl iodide, and the product decomposed by 30% sulphuric acid; the required hydrocarbon was thus obtained with b. p. 132.5—134.5°,  $d_4^{20}$ : 0.8378 (Sabatier gives b. p. 132°,  $d_4^{20}$ : 0.8411). Its hydrogenation gave a very interesting result. Using small amounts, we observed only two sections in its curve (Fig. 3, Curve 1), the first corresponding to 44% of the total volume of hydrogen absorbed, but with larger amounts (Curve 2) we found three distinct sections, the first part of the curve showing an additional break, which would have corresponded to only 10—11 c.c. in Curve 1 and would therefore escape notice. The absorptions in the three sections are 7, 37, and 56%

respectively of the total. The explanation of these breaks is as follows. The dehydration of 1:2-dimethylcyclohexanol by sulphuric acid can occur in three directions, resulting in the formation, in successively decreasing yield, of the following three hydrocarbons :



Now, from the types to which they belong, it is seen that their ease of hydrogenation should be in the reverse order, the compound of Type IIas being reduced preferentially. In order to assure ourselves that the second section of the Curve 2 corresponds to the hydrogenation of the second compound, we hydrogenated a mixture of our hydrocarbon with terpineol. The curve obtained is shown in Fig. 6 (Curve 2). Owing to the small amount of hydrocarbon taken, we can discern only two portions in it, but the first has increased in agreement with the amount of terpineol used, proving that the linkings hydrogenated in this section are both of Type IIIc.

It is clear that the hydrocarbon was too impure for use as a standard compound of Type IVc, so, since the impurities (Types IIas and IIIc) are hydrogenated preferentially, the mixture was allowed to absorb 45% of the maximum hydrogen, whereby we obtained a mixture of saturated hydrocarbons together with the (presumably) unchanged hydrocarbon of Type IVc, which we used in subsequent experiments as a comparative standard of 55% content.

The foregoing results for individual cyclic hydrocarbons are completely analogous to those for open-chain compounds (Part I), and indicate that the absorption rates of the Types IIc, IIIc, and IVc decrease in that order. Moreover, the curves of the last two types fall slowly, although that of Type IIIc shows a slight rise initially; on the other hand, the curves for compounds of Type IIc (except indene) tend to be horizontal, pointing to a constant absorption rate.

#### *Hydrogenation of Mixtures of Cyclic Ethylenic Derivatives (Table II).*

*Mixtures of Compounds of the Same Degree of Substitution.*—  
(a) Type IIc (Fig. 3). We examined two binary mixtures in this category, viz., cyclohexene + 1-methyl- $\Delta^3$ -cyclohexene (Curve 3) and cyclohexene + indene (Curve 4). In each case both components were hydrogenated concurrently, the curves showing no breaks. The curve of the first mixture is nearly horizontal, whereas that of the second slopes somewhat as in the case of indene alone. The second mixture is interesting in that it suggests that the effect of

platinum-black is similar whether a 5- or a 6-membered ring is involved.

TABLE II.

Compound.	Fig. and curve Nos.	Amount, g.	Temp. and press. of H <sub>2</sub> .	H <sub>2</sub> absorbed, c.c.	
				Calc.	Found.
{ <i>cyclo</i> Hexene	3; 4	0.8676	17°; 762 mm.	223	337 353
{ Indene		0.6085		114	
{ 1-Methyl- $\Delta^3$ - <i>cyclo</i> -hexene	3; 3	0.5455	18°; 749	137.5	442.5 438.5
{ <i>cyclo</i> Hexene		1.148		305†	
{ Carvotanacetone	4; 1	0.926	21°; 764	146	228 221
{ Terpineol		0.526		82	
{ Carvone	4; 2	1.0000	20°; 755	324	530 525
{ <i>l</i> -Limonene		0.5786		206	
{ <i>l</i> -Limonene	4; 3	0.8175	21°; 752	294	367 383
{ Terpineol		0.4585		73	

† Based on content of 90% (see p. 323).

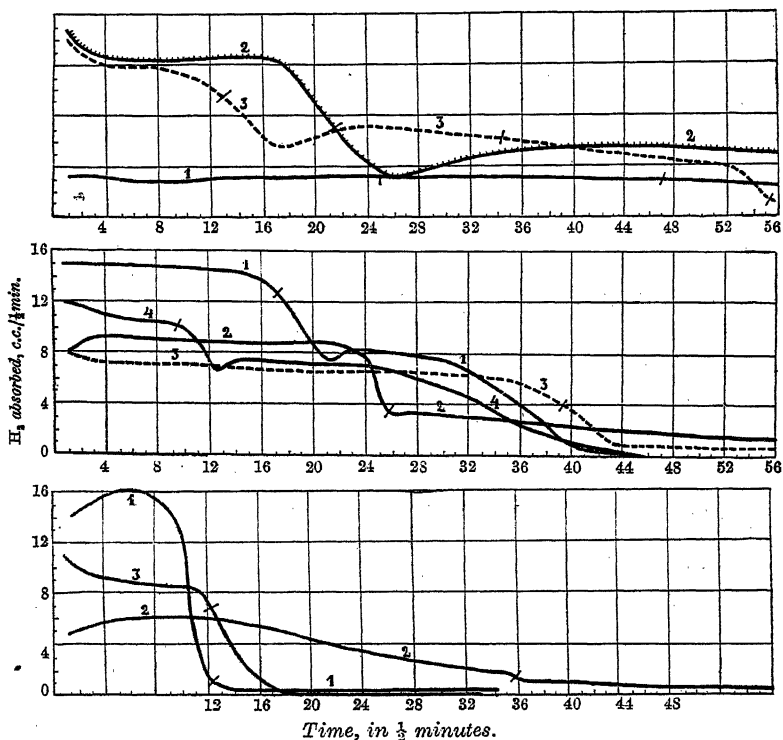
(b) Type IIIc (Fig. 4). Three such mixtures were examined: carvotanacetone + terpineol (Curve 1), carvone + *l*-limonene (Curve 2), and *l*-limonene + terpineol (Curve 3). The general character of the absorption curve of the first mixture is similar to that of the individual curves of its components; it has no breaks, and apparently both components are hydrogenated concurrently. The mixture of carvone + *l*-limonene corresponds to two binary mixtures, Type IIas as well as Type IIIc being present in each compound. The curve resembles those of the two components separately, and calculation shows that the only break corresponds with complete hydrogenation of the two Type II bonds, followed by simultaneous reduction of the bonds in the ring of each compound. We have no doubt that reduction occurs in this order, for 50% hydrogenation of carvone and of *l*-limonene produces carvotanacetone and carvomenthene respectively (Vavon; Armstrong; *loc. cit.*).

The curve for *l*-limonene + terpineol is similar to the preceding case, the stages being the hydrogenation of the bond of Type II, the abrupt fall in the rate to the minimum, and hydrogenation of the cyclic bonds simultaneously. The curve shows also the beginning of a third section, corresponding, apparently, to the very slow hydrogenation of the alcoholic group of terpineol.

*Hydrogenation of Mixtures of Cyclic Ethylenic Derivatives of Different Degrees of Substitution* (Table III).—(a) Types IIc + IIIc (Fig. 5). We examined six binary mixtures of this type, *viz.*, (1) *cyclo*hexene + carvotanacetone (Curve 1); (2) *cyclo*hexene + terpineol (Curve 2); (3) indene + terpineol (Curve 3); (4) 1-methyl- $\Delta^3$ -*cyclo*hexene + terpineol (Curve 4); (5) *cyclo*hexene + carvone; and (6) *cyclo*hexene + *l*-limonene. The last two, being combinations

of Types IIas + IIc + IIIc, are discussed under the head of mixtures of Types IIas + IIc (see p. 331). The curves of the other four mixtures are all similar, showing, first, the constant or slightly falling hydrogenation of Type IIc, then the abrupt fall to the minimum,\* and finally the slow fall characteristic of the hydrogenation of the compound of Type IIIc. The different sections of these curves are very similar to the curves for the individual components of the mixtures; moreover, each component retains its own rate of

FIGS. 4, 5, 6.



hydrogenation fairly closely, except that in the mixture indene + terpineol, the latter reacts much more slowly than when alone. Further, the breaks on the curves of these mixtures are much more pronounced than in the case of the corresponding open-chain mixtures (compare Part I, *loc. cit.*).

(b) Types IIc + IVc (Fig. 6). We examined only one mixture of this type, *viz.*, cyclohexene + 1:2-dimethyl- $\Delta^1$ -cyclohexene (Curve 1).

\* The minimum rate is not noticeable in the mixture indene + terpineol, probably because of the decreased absorption rate of the latter.

As expected, *cyclohexene* is hydrogenated first, and then the rate falls extremely sharply to a very small fraction ( $\frac{1}{60} - \frac{1}{90}$ ) of its value to that characteristic of the reduction of the other compound.

TABLE III.

Compound.	Fig. and curve Nos.	Amount, g.	Temp. and press. of H <sub>2</sub> .	H <sub>2</sub> absorbed, c.c.	
				Calc.	Found.
<i>cyclohexene</i>	5; 1	0.943	16°; 752 mm.	*248	377 390
Carvotanacetone		0.888		129	
<i>cyclohexene</i>	5; 2	0.811	14°; 762	*209	315 304.5
Terpineol		0.6955		106	
Indene	5; 3	1.346	18°; 760	†258	358 359
Terpineol		0.646		100	
1-Methyl-Δ <sup>3</sup> - <i>cyclohexene</i>	5; 4	0.438	16°; 765	105	266 276
Terpineol		1.052		161	
<i>cyclohexene</i>	6; 1	0.6174	17°; 765	*160	195 173‡
1:2-Dimethyl-Δ <sup>1</sup> - <i>cyclohexene</i>		0.294		§35	
Carvotanacetone	6; 3	0.6859	18°; 760	108	143 128‡
1:2-Dimethyl-Δ <sup>1</sup> - <i>cyclohexene</i>		0.2898		§34.6	
Terpineol	6; 2	0.9524	17°; 765	146	182 179‡
1:2-Dimethyl-Δ <sup>1</sup> - <i>cyclohexene</i>		0.3056		§36	

\* Based on a content of 90% (see p. 323).

† Process incomplete.

‡ Based on a content of 93%. § Based on a content of 55% (see p. 326).

(c) Types IIIc + IVc (Fig. 6). Two of these mixtures were studied: 1:2-dimethyl-Δ<sup>1</sup>-*cyclohexene* with terpineol (Curve 2) and with carvotanacetone (Curve 3). The break in the curve for the first mixture was not pronounced, but that for the second was very sharp. The hydrogenation rate of carvotanacetone was nearly double its usual value, and it will be seen later that the reduction of tetramethylethylene is similarly accelerated in the presence of 1:2-dimethyl-Δ<sup>1</sup>-*cyclohexene*.

The results obtained with these mixed cyclic ethylenic derivatives show that the two components are hydrogenated concurrently if they are of a similar degree of substitution, or consecutively and at different rates if of different degrees; the corresponding curves are accordingly continuous or discontinuous, respectively. The ease of hydrogenation decreases according to type in the order IIc, IIIc, IVc, in conformity with the results obtained for open-chain compounds (Part I) and for individual cyclic compounds.

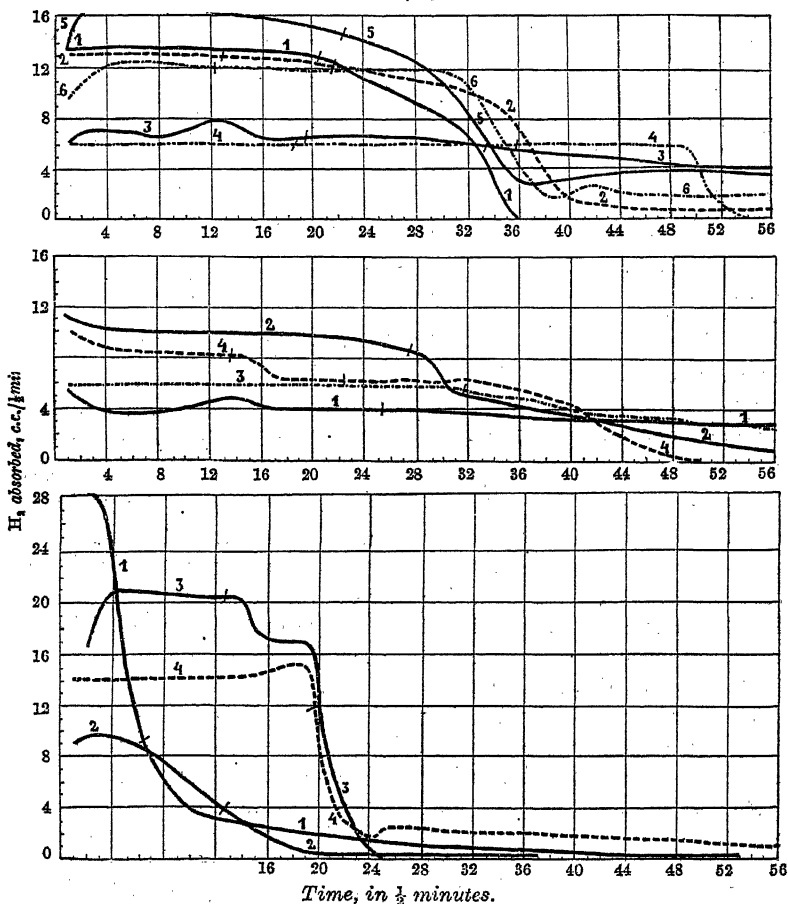
#### *Hydrogenation of Mixtures of Cyclic with Open-chain Ethylenic Derivatives.*

The results obtained in this series of experiments show that here again the degree of substitution determines the character of the hydrogenation. They also show that platinum-black acts differently

upon similarly substituted derivatives of open-chain and of cyclic structure during the hydrogenation of their mixtures.

(1) *Compounds of the Same Degree of Substitution* (Table IV).—  
(a) Types IIc + II<sub>s</sub> (Fig. 7). In each of the three mixtures, *cyclohexene* + *anethole* (Curve 1), *1-methyl-Δ<sup>3</sup>-cyclohexene* + *anethole*

FIGS. 7, 8, 9.



(Curve 2), and *cyclohexene* + *cinnamyl alcohol* (Curve 3), the components are hydrogenated at the same rate, the curves having no sharp breaks. The curves of the first two mixtures are very much like that of *anethole*.

(b) Types IIc + II<sub>as</sub> (Fig. 7). We examined three mixtures, *viz.*, those of *cyclohexene* with *camphene* (Curve 4), with *carvone* (Curve

TABLE IV.

Compound.	Fig. and curve Nos.	Amount, g.	Temp. and press of H <sub>2</sub> .	H <sub>2</sub> absorbed, c.c.	
				Calc.	Found.
{ <i>cyclo</i> Hexene	7; 1	1.0194	19°; 764 mm.	*267	386 385.5
{ Anethole		0.7400		119)	
{ 1-Methyl- $\Delta^3$ - <i>cyclo</i> -hexene	7; 2	0.6458	16°; 750	162	435.5 439
{ Anethole		1.685		273.5)	
{ <i>cyclo</i> Hexene	7; 3	0.5673	19°; 768	*147	365 395
{ Cinnamyl alcohol		1.236		218)	
† { <i>cyclo</i> Hexene	7; 5	1.317	19°; 764	*345	611 595
{ Carvone		0.836		266)	
{ <i>cyclo</i> Hexene	7; 4	0.7779	20°; 762	*204	308 297
{ Camphene		0.5909		104)	
{ <i>cyclo</i> Hexene	7; 6	1.075	18°; 765	*280	543.5 528
{ <i>l</i> -Limonene		0.7556		263.5)	
{ Carvotanacetone	8; 1	1.3953	21°; 765	220	325 329
{ Methylheptenone		0.5533		105)	
{ Terpineol	8; 2	0.6324	19°; 765	98	365 373
{ Mesityl oxide		1.0993		267)	
{ Terpineol	8; 4	1.132	18°; 745	179	301 300
{ Methylheptenone		0.6334		122)	
† { Carvotanacetone	8; 3	0.6883	18°; 764	107	318 305
{ Mesityl oxide		0.8714		211)	
§ { 1:2-Dimethyl- $\Delta^1$ - <i>cyclo</i> hexene	9; 1	0.6092	17°; 778	†70.5	205 200
{ Tetramethylethylene		0.4871		134.5)	
Same mixture	9; 2	0.1401	17°; 778	†16.5	115.5 121
		0.3500		99)	

\* Based on a content of 90% (see p. 323).

† Bath temperature, 17°.

‡ Based on a content of 55% (see p. 326).

§ For this expt. 1 g. of platinum-black was used.

5), and with *l*-limonene (Curve 6). The hydrogenation rate of the first mixture is constant throughout the whole reaction. The other two mixtures are each a combination of the types IIc + IIas + IIIc; the disubstituted compounds are hydrogenated together, the absorption rate being nearly constant. The end of the hydrogenation of the system IIc + IIas coincides with a sharp fall in the absorption rate, which reaches a minimum and then increases a little.

(c) Types IIIc + III (Fig. 8). Four mixtures were examined: carvotanacetone + methylheptenone (Curve 1), mesityl oxide + terpineol (Curve 2), mesityl oxide + carvotanacetone (Curve 3), and terpineol + methylheptenone (Curve 4). The curves of the two mixtures containing mesityl oxide have prominent breaks, for this compound is hydrogenated first and at an almost constant rate. The mixture of terpineol + methylheptenone is of interest because the break in the curve does not coincide exactly with the end of the hydrogenation of either of the components. Each section seems to correspond with the hydrogenation of a mixture of the two components in different proportions, and the size of the sections suggests

that methylheptenone probably predominates in the first portion. This anomaly is still more prominent in the pair methylheptenone + carvotanacetone: the break is not sharp and is strikingly displaced to the left. The resemblance between curves 1 and 4, on the one hand, and between curves 2 and 3, on the other, is noteworthy. It is clear that sometimes the shape of the curves depends, not only upon the characteristics of the type, but also on those of the individual.

These examples show that in the hydrogenation of their mixtures, compounds of the types III and IIIc are not equivalent. Apparently platinum-black absorbs the open-chain type preferentially and consequently compounds of this type are usually hydrogenated first.

(d) Types IVc + IV (Fig. 9). The mixture, 1:2-dimethyl- $\Delta^1$ -cyclohexene + tetramethylethylene (Curves 1 and 2) was studied, 1 g. of platinum-black (instead of the usual 0.2 g.) being used at first because both these hydrocarbons are hydrogenated very slowly. Two experiments showed abnormal reactivity on the part of the tetramethylethylene (Curve 1). Using only 0.2 g. of platinum-black, we obtained Curve 2, where again the end of the hydrogenation of tetramethylethylene is sharply defined and the reaction rate is abnormal, being 9.5 c.c./ $\frac{1}{2}$  min.

(2) *Compounds of Different Degrees of Substitution* (Table V).—

(a) Types IIc + I (Fig. 9). In the binary mixture, saffrole + cyclohexene (Curve 3), the former was hydrogenated first, at an almost constant rate, and the sharp break on the curve coincides closely with the end of this process.

(b) Types IIc + III (Fig. 10). We examined four mixtures: cyclohexene + mesityl oxide, cyclohexene + methylheptenone (Curve 1), cyclohexene + trimethylethylene (Curve 2), and indene + methylheptenone. In all four, the cyclic compound was hydrogenated first; the breaks were somewhat like those in the mixtures of Types IIc + III and IIas + III (Part I, *loc. cit.*), and much less well-defined than those in the curves of mixtures of Types IIc + IIIc and IIas + IIIc. This difference can be explained by the fact (see above) that Type III is much more readily adsorbed by platinum-black, and therefore more readily hydrogenated, than IIIc; hence Type III is more nearly allied to Type IIc than to Type IIIc.

In the mixture, cyclohexene + mesityl oxide, we have a very complicated case, owing to the presence of the conjugated system in the latter; it seems that cyclohexene is hydrogenated first. This curve, as well as that of the mixture indene + methylheptenone, is not given here.

(c) Types IIc + IV (Fig. 10). We examined the binary mixture cyclohexene + tetramethylethylene (Curve 3); the former is hydrogenated first at a constant rate, and a sharp break divides this



process from the reduction of the other component, which, however, is markedly higher than normally.

FIGS. 10, 11.

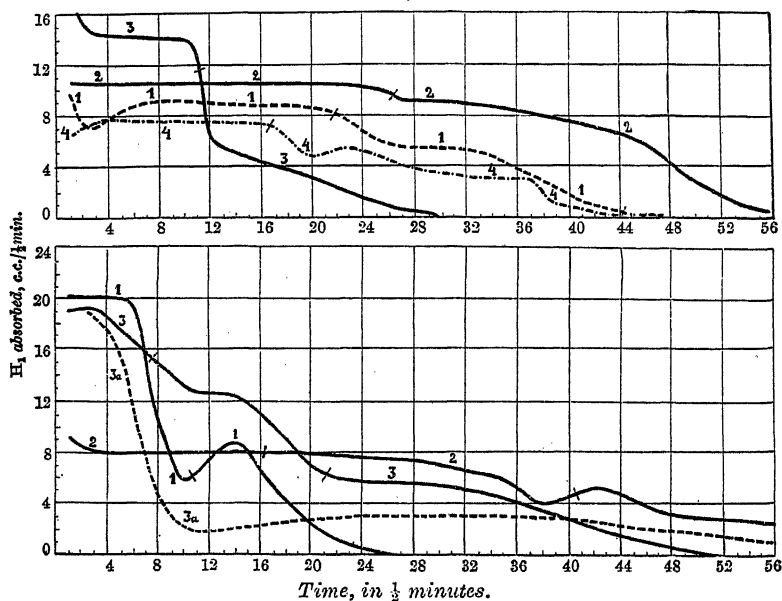


TABLE V.

Compound.	Fig. and curve Nos.	Amount, g.	Temp. and press. of H <sub>2</sub> .	H <sub>2</sub> absorbed, c.c.	
				Calc.	Found.
Safole	9; 3	1.517	18° 758 mm.	*131	355 367
cycloHexene		0.501		275.5	
Safole	9; 4	1.844	18° 750	92	367.5 365
Terpineol		0.5875		*181	
cycloHexene	10; 1	0.6836	21° 760	87	268 280
Methylheptenone		0.4538		*268	
cycloHexene	10; 2	1.019	19° 757	158	426 434
Trimethylethylene		0.459		*153	
cycloHexene	10; 3	0.5848	19° 765	*58	211 206.5
Tetramethylethylene		0.2036		116	
Terpineol	10; 4	0.7468	19° 762	79.5	195.5 206
Tetramethylethylene		0.2796		164	
Camphene	11; 1	0.9309	19° 758	69	233 225
Terpineol		0.4426		165	
Camphene	11; 2	0.9200	18° 742	250	415 371
l-Limonene		0.6973		264	
Carvone	11; 3	0.8232	17° 753	157	421 386
Camphene		0.8859			

\* Based on a content of 90% (see p. 323).

(d) Types IIIc + I (Fig. 9). In the mixture safole + terpeneol (Curve 4), the former is hydrogenated first and at a constant rate,

slightly increasing towards the end. The curve then falls sharply to a minimum, and the reduction of terpineol sets in with a slight rise followed by a gradual fall.

(e) Types IIIc + IIas (Fig. 11). This category is illustrated by 7 curves: (1) carvone, (2) *l*-limonene, (3) carvone + *l*-limonene, (4) terpineol + *l*-limonene, (5) camphene + terpineol (Curve 1), (6) camphene + *l*-limonene (Curve 2), and (7) camphene + carvone (Curves 3 and 3a). The curves for the first four reductions have already been given (Fig. 2, Curves 1 and 2; Fig. 4, Curves 2 and 3), since the simpler systems also contained those of the type now concerned. The mixtures of camphene with *l*-limonene and with terpineol gave curves of the same type: the minimum is very pronounced, particularly in the second case.

The mixture carvone + camphene is noteworthy. Its curve has three sharply separated sections corresponding with the hydrogenation (i) of the side chain of carvone, (ii) of camphene, and (iii) of the double bond in the ring of carvone (Curve 3). This is the first case in which a break has been found in the hydrogenation of a mixture of two bonds both of the type IIas; and it is quite unexpected, for carvone behaved like camphene in all the hydrogenations of mixtures, and it would be anticipated that the bonds in the side chains of carvone and camphene would be equivalent in respect to platinum-black when hydrogenated in presence of one another. In this case, evidently, the course of hydrogenation is chiefly determined, not by the degree of substitution at the double bond in the compounds, but by their individual qualities and their mutual influence on adsorption at the surface of the catalyst. We therefore made the following experiment. Immediately after the mixture of carvone + camphene had been reduced, a certain amount of carvone was introduced into the hydrogenation vessel, and the course of its reduction followed (Curve 3a). Comparison of Curves 3 and 3a shows that the rate of reduction of the nuclear bond (Type IIIc) of carvone is decreased in the second case: the reduction of its side chain is abnormally rapid in both cases.

(f) Types IIIc + IV (Fig. 10). In the mixture terpineol + tetramethylethylene (Curve 4), the latter is attacked first; the break is clearly visible, and the curve has a minimum. The third section of the curve corresponds with the hydrogenation of the alcoholic group of terpineol.

A general survey of our experiments establishes that the degree of substitution at a double bond is the chief factor determining the order and character of the hydrogenation of mixtures of ethylenic derivatives (either cyclic or open-chain). Other factors, as, for instance, the individual characteristics of the molecules or the

mutual influence of molecules of two different species on their adsorption (and hydrogenation) at the surface of platinum-black, predominate only in exceptional cases. Such phenomena occur only when one of the components of a mixture contains conjugated double bonds, as in mesityl oxide or carvotanacetone. The hydrogenation of individual compounds containing this system is anomalous, and the presence of such a component in a mixture changes the whole character of the hydrogenation.

### *Conclusions.*

(1) Cyclic disubstituted ethylenic derivatives are hydrogenated more readily than trisubstituted ones, and these, in turn, more readily than tetrasubstituted.

(2) Mixtures of cyclic ethylenic derivatives of a similar degree of substitution are hydrogenated at a common rate, the curves showing the absorption of hydrogen being continuous.

(3) In mixtures of cyclic ethylenic derivatives of different degrees of substitution, the components are hydrogenated consecutively in the order given in (1). The curves for such mixtures always have breaks, corresponding closely to the end of the hydrogenation of the first component, and in many cases being associated with a minimum in the rate of reaction.

(4) In a mixture, the section of the curve corresponding to the hydrogenation of any one component bears a strong resemblance to the curve obtained when this component is hydrogenated alone.

(5) The individual hydrogenation rates of the compounds may be considerably modified in mixtures.

(6) The hydrogenation of mixtures of cyclic with open-chain ethylenic derivatives of the same degree of substitution proceeds on the following lines. (a) In mixtures of cyclic with open-chain (*s.*- or *as.*-) disubstituted compounds, the components are hydrogenated concurrently, the curves for such mixtures being continuous. (b) In mixtures of cyclic with open-chain trisubstituted compounds, the components are hydrogenated consecutively, the latter reacting preferentially in virtue of a somewhat greater capacity for adsorption by platinum-black; the hydrogenation curves of such mixtures show rather considerable breaks. (c) In mixtures of a cyclic and an open-chain tetra-substituted compound, the latter is hydrogenated considerably more rapidly than the former.

(7) Mixtures of cyclic or open-chain (*s.*- or *as.*-) disubstituted compounds with cyclic tri- or tetra-substituted compounds show much sharper breaks in their hydrogenation curves than when the more heavily substituted compounds are open-chain.

(8) Mixtures of cyclic with open-chain ethylenic derivatives of

different degrees of substitution are usually hydrogenated consecutively, the component with the lower degree of substitution at the double bond being hydrogenated first.

(9) In mixtures containing a component with a conjugated system, deviations from the above generalisations are observed.

(10) Anhydrides of maleic and citraconic acids, unlike the acids themselves, are toxic towards platinum-black.

(11) Examination of the hydrogenation curves of mixtures of cyclic ethylenic derivatives of known constitution (standard derivatives) with those of unknown constitution enables us to determine the type of substitution at the double linking in the latter, but it is essential that the standards be cyclic.

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## XLIX.—On Active Nitrogen. Part VII. Further Studies upon the Decay of the Nitrogen After-glow.

BY ERIC JOHN BAXTER WILLEY.

IN previous papers (Part V; J., 1928, 1620; see also 1929, 228) it was shown that the ternary reaction  $2N + N_2 \longrightarrow 2N_2$  (+ glow) would provide, upon a simple kinetic basis, a quantitative explanation of (i) the long life of the nitrogen after-glow, (ii) the negative temperature coefficient of the decay, and (iii) the amount of the chemically active species present under given conditions. Experimental work showed, however, that the process was to be represented as  $2N + 2N_2 \longrightarrow 3N_2$ , rather than as the simpler ternary reaction given above. It has, moreover, been concluded that the luminosity and chemical activity are closely related, and not independent, as suggested formerly (Part IV; J., 1927, 2831), and that it is not improbable that the chemically active species, which persists after the glow has been destroyed either by heat or by an electric discharge (Part IV; *loc. cit.*), represents a molecule which has acquired part of the energy of association of atoms recombining in a three-body process.

Shortly after Part V appeared, Kneser showed (*Ann. Physik*, 1929, 87, 717) that the effects of pressure upon the decay of the after-glow are in agreement with the three-body theory; he also concluded, in agreement with Lord Rayleigh (*Proc. Roy. Soc.*, 1912, A, 86, 262), that the walls may exert a considerable influence upon the reaction, but that the process is usually homogeneous, and that the Kaplan-Cario theory of the nature of active nitrogen is not in

disagreement with these findings. Herzberg also has (*Z. Physik*, 1928, 46, 578) emphasised the probable part played by the walls in the after-glow phenomena. The present author has suggested that the discrepancy between the two investigations might be due to different experimental conditions, and that a surface reaction occurring simultaneously with that in the gas phase masked the true homogeneous decay which it was desired to measure.

An unsatisfactory feature of both investigations was the measurement of the glow intensities by direct visual methods, a personal factor thus being introduced. It appeared advisable, therefore, to study the matter more completely, with special reference to any possible wall reaction which might enter. Bonhoeffer and Kaminsky (*Z. physikal. Chem.*, 1927, 127, 385) have concluded that the spectrum of the after-glow is independent of the nature of the impurity which, as is well known, must be present to cause nitrogen to develop its glow when sparked, and the view has gained ground that these "photogens" (as they may be termed) "poison" the walls and prevent recombination of atoms thereupon, the case being analogous to that of atomic hydrogen, whose life in "wet" vessels is much longer than in "dry" ones. If this theory be correct, a quantitative relation will exist between the decay mechanism and the purity of the nitrogen employed for any one vessel; it was decided to examine this point experimentally and to measure the glow by means of a photo-cell, the personal factor thus being eliminated.

#### EXPERIMENTAL.

*Apparatus.*—This was similar to that employed in the author's earlier investigation, save (i) that additional drying tubes were provided, together with an extra large trap, cooled by liquid air, through which the nitrogen passed after leaving the purification system, and (ii) that inlets were provided both (A) above and (B) below the discharge for admission of other gases as desired. The discharge, some 30 cm. long, burned between water-cooled aluminium electrodes; a condenser of 0.0125 microfarad was shunted across the spark gap, and the r.m.s. current was about 30 milliamps. The observation tube and manometer were built into a sheet-iron box (5' × 3' × 3'), with black cloth curtains on the front, and all precautions were taken to keep the observation cabinet light-tight, and to prevent light from the spark entering the observation tube, which was 60 cm. long and 2.5 cm. wide.

*Nitrogen.*—Preliminary experiments showed that after phosphorus has been in use for a fortnight or so to remove oxygen from the nitrogen, it becomes very slow in action, and about 0.03% of the gas escapes absorption, unless contact is very prolonged. Copper

at 600° gave a gas which was found, by addition of other gases through inlet A (the photogen feed tap) and observation of their effects upon the glow, to contain *ca.* 0.3% of argon (which did not appear to have any influence) and less than 0.01% of other gases, and to give little or no glow. It was therefore employed as the standard "pure" gas, and the use of phosphorus was discontinued.

*Measurement of Glow Intensity.*—The photographic method, with ordinary plates, was valueless, since the  $\alpha$ -bands were not recorded by reason of their long wave-length, while the number of observations to be made rendered the adoption of panchromatic plates inadvisable.

Attempts were therefore made to measure the luminosity by photoelectric methods, the phosphorus method of purification being temporarily used to obtain a gas which gave a strong glow. The ordinary potassium photo-cell is practically insensitive to yellow light,\* and when such a cell was employed, the photo-currents were found to be of the order of  $10^{-11}$  amp., even with strong glows. Such currents can be measured (a) by observing by means of a quadrant electrometer the fall in potential across an alcohol-xylene resistance of *ca.*  $10^{11}$  ohms; (b) by means of a Paschen or Downing galvanometer directly in circuit; or (c) by applying the potential obtained by method (a) to a valve amplifier specially constructed to deal with such cases—devices such as that of Wynn-Williams are admissible only with larger currents. When any one of these methods was tried, great difficulties were encountered owing to the discharge which produced the active nitrogen setting up a diversity of electromagnetic disturbances which necessitated the most rigorous shielding; the movement of a photo-cell along a tube through which active nitrogen was being streamed required flexible leads, and the difficulties were thus at once increased.

The method adopted after numerous failures was rendered possible through the kindness of Mr. C. F. Trippe, and the British Thomson Houston Co., Ltd., who placed at the author's disposal two special caesium cells having an emission some 50 times that of the best cell of any other type which was tried. These were placed in parallel and fitted in series with (a) a Tinsley moving-coil galvanometer of sensitivity  $5 \times 10^{-10}$  amp., and practically constant zero, and (b) a high-tension accumulator giving 130 volts; practically no "dark" current was obtained, and calibration experiments using an ordinary optical bench method showed that the deflexion of the galvanometer was directly proportional to the brightness of the light incident upon the cells. For the actual experiments,

\* Ordinary caesium cells have a much greater emission for yellow light, but are very unsatisfactory for quantitative work.

these were fixed in a light wooden frame held in a retort stand provided with a pointer on the base, and fitted to slide between rails parallel to and underneath the horizontal observation tube; the rails carried a scale, and the zero point was chosen some 10 cm. along the tube and 5 cm. downstream from the side limb B (see above).

*Procedure.*—For measurements of the glow, the cells were first placed at the zero point and screened from the light by means of a black cloth. The galvanometer reading was taken, and the cloth withdrawn to cause the cells to become illuminated; the second reading was then made, the instrument being practically dead-beat and coming to rest in 30 secs. or so. This was then repeated with the cells at the 5, 10, 15, 20, 25, etc., points until the deflexion became less than 0.3 cm., after which further measurements were made at the 22.5, 17.5, 12.5, 7.5, and 2.5 cm. points, some 15–20 observations being made for each run according to the glow intensity. The data were then plotted as the reciprocal of the square root of glow intensity against distance along the observation tube; for a reaction which is bimolecular with respect to the glow-producing system, a linear relation should thus be obtained (see, *e.g.*, Willey, *loc. cit.*).

### Results.

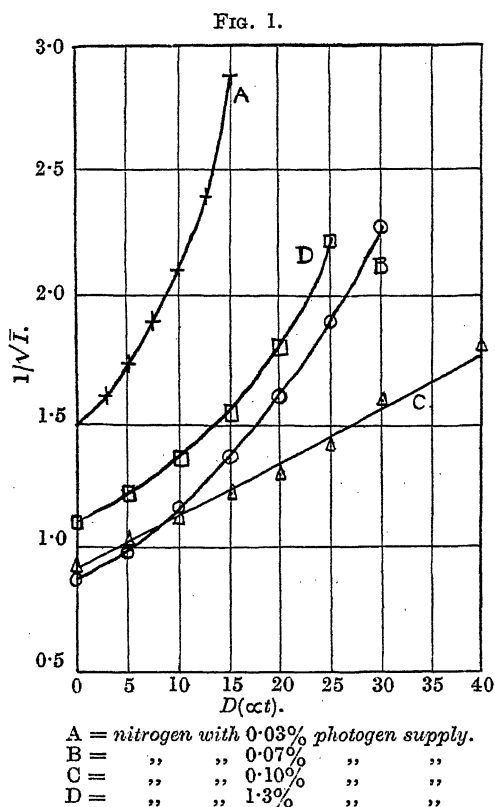
*The Production of a Glow in Pure Nitrogen.*—It was found that with the hot-copper method of purifying nitrogen and with the trap well cooled by liquid air, the faint glow visible in the nitrogen at first quickly diminished until the gas was quite non-luminous as it passed along the observation tube. Moreover, entirely negative results were obtained in attempts to detect chemical activity in the nitrogen by means of nitric oxide admitted at B, the peroxide being tested for according to the method previously described (Part IV). It appears then that nitrogen which is so pure as to give no glow is not chemically active.

*Glow Phenomena.*—The after-glow could easily be developed either by reducing the temperature of the copper or by the addition of small amounts of other gases through the photogen feed tap. The results of systematic investigation of the effect of added impurity are now given;  $I$  is the intensity of the glow, and  $t$  the time, which is proportional to  $D$ , the distance along the observation tube.

(a) *Form of the  $1/\sqrt{I}-t$  graph.* ( $\alpha$ ) With fairly pure nitrogen the line is strongly curved (Fig. 1, A), becoming less so with continued increase of photogen (Fig. 1, B) until it passes through a linear form (Fig. 1, C), and then again becomes curved (Fig. 1, D). This shows that the apparent "order" of the decay reaction is dependent upon the purity of the nitrogen employed. The points

for Fig. 1, A give a fairly straight line when plotted as  $\log I$  against  $D$ , indicating a decay reaction of approximately the first order.

( $\beta$ ) During a series of experiments which had as their object the determination of the relation between glow intensity and concentration of chemically active species, the following measurements were taken : (i) Decay curve (Fig. 2, A) ; (ii) three estimations of the chemically active species ; (iii) 20 minutes after this, a further



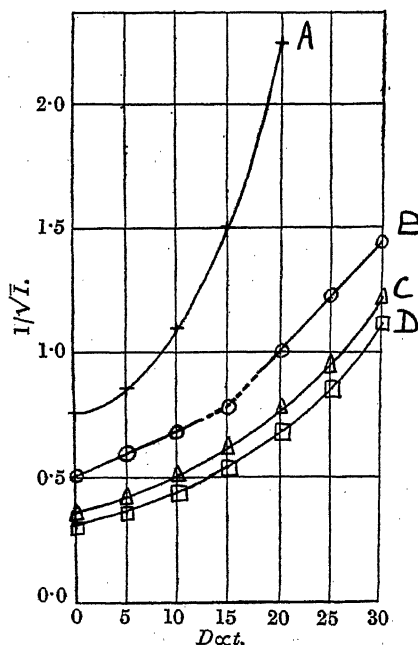
decay curve (Fig. 2, B) ; and finally (iv) three more analyses. During runs (i) and (iii), the nitric oxide stream was replaced by an equal one of pure nitrogen to keep the pressure constant, and the flow of gases and the spark were maintained throughout. It will be seen that the graphs are linear after the first few cm. but vary widely in slope ; in spite of this the same amount of chemically active nitrogen was found in all six cases. Hence it follows that a stream of luminous nitrogen may decay at widely different rates although it contains the same amount of the chemically active form throughout.

( $\gamma$ ) In another experiment a decay curve (Fig. 3, A) was plotted for fairly pure nitrogen (*ca.* 0.03% of oxygen being used as photogen), and the photogen concentration then increased to *ca.* 0.07%, after which Fig. 3, B was obtained. The apparatus was allowed to function for 90 minutes, and a further decay curve (3, C) obtained ; the observation tube was then flamed gently, the gases and spark being shut off and a vacuum of 0.0001 mm. maintained. After cooling, the gases were readmitted, the spark was run for 90 minutes, and curve 3, D was obtained.



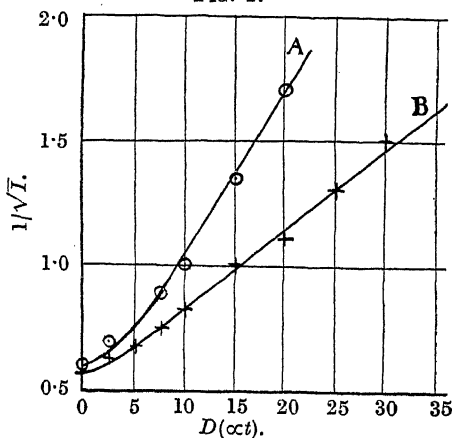
( $\delta$ ) The clearest explanation of the results described in sections ( $\alpha$ ), ( $\beta$ ), and ( $\gamma$ ) is that they are due to wall effects. With nitrogen of a high degree of purity the walls are so clean that recombination of the atoms, assured now, as before, to be the primary glow-producing elements, occurs with great ease; adopting the author's earlier view (Part V) as to the origin of the chemical activity, the failure to obtain this in the absence of photogens is also readily explained, and is discussed later in the light of the Kaplan-Cario theory. The findings given in ( $\alpha$ ) arise from the progressive poisoning of the walls by the

FIG. 3.



primary glow-producing system, the slope of the curve is not determined solely by total gas pressure, as it should be for a reaction

FIG. 2.



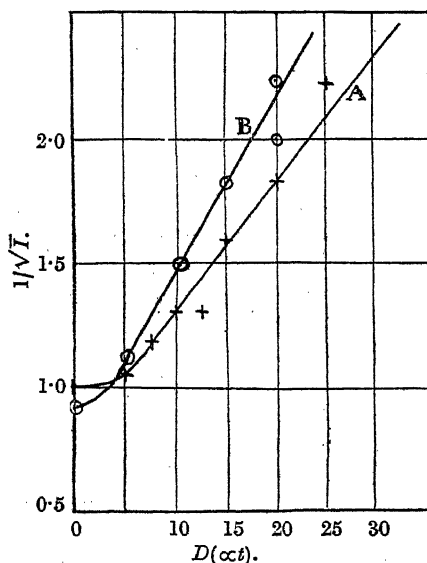
photogen until probably a point of minimum wall activity is reached when the reaction becomes homogeneous and bimolecular (with respect to the glow-producing elements) as in Fig. 1, C, while in 1, D too much photogen is present and is influencing the gas phase reaction either by direct participation in the glow emission process or else possibly by reaction with the chemically active species.

In Fig. 2, B we have shown the influence of an adsorbed nitric oxide film upon the decay rate of the glow: it is much reduced, as would be expected. Furthermore, while the linear nature of the graph shows that the reaction is binary with respect to the

$2N + N_2 \longrightarrow 2N_2$ , when the condition of the walls necessitates their being taken into account. A more important phenomenon is the constancy of the chemical activity, suggesting that if, as the Kaplan-Cario theory indicates, the active species is a participant in the glow emission reaction, it has as a complement a substance which is very susceptible to wall influence (see later).

The results given in Fig. 3 are in striking agreement with the wall-effect hypothesis. Fig. 3, A has as its fellow Fig. 1, A, while at the time when 3, B was obtained sufficient photogen had entered the observation tube to poison the walls only so far along the direction of flow as the point of inflexion, and the practical

FIG. 4.



1900 C.c. of nitrogen per hour at N.T.P.

A = Decay curve for 4.6 mm.

B = " " " " 6.8 "

coincidence of 3, C and 3, D shows that they represent the final state of the walls for nitrogen of this particular degree of purity. No marked effect of the photogens upon the electrical conditions has yet been observed, and the findings in Fig. 3 cannot be attributed to progressive changes in the bulk composition of the gas, since the very small volume between the photogen inlet and the observation tube, taken in conjunction with the high flow-speed of the gas at the pressure employed (4.6 mm.), rules it out of consideration.

(e) The evidence presented in sections ( $\alpha$ ), ( $\beta$ ), ( $\gamma$ ), and ( $\delta$ ), that the condition of the

walls determines very largely the mechanism of the decay of the nitrogen after-glow, may be tested in the following manner. The activity of the surface may be expected, *ex hypothesi*, to be proportional to the area exposed; the more the gas adsorbed upon it, the less will it influence the decay, provided that reaction does not occur between the adsorbed film and the glow-emitting system. The simplest way of decreasing the wall effect without introducing any such complication is clearly to employ nitrogen as a photogen, i.e., by raising the over-all pressure to increase the adsorption of molecular nitrogen; if the departure from linearity in the

$1/\sqrt{I}-t$  graph is due to wall effects, the curves should be straightened in progressive runs from low to high pressures. This effect may readily be observed and is shown in Fig. 4.

(b) *The triple-collision hypothesis.* Assuming the glow emission to result from a reaction  $2N + N_2 \rightarrow 2N_2$ , it follows that for a constant concentration of N the initial intensity will be increased and the life of the glow diminished by addition of  $N_2$ . Kneser (*loc. cit.*) confirmed this deduction, but Bonhoeffer and Kaminsky (*loc. cit.*) dissented from it. The probability of the after-glow resulting from a three-body reaction has already been discussed (Part V, J., 1928, 1620; 1929, 228) and the balance of evidence considered to be in its favour; it will now be shown (i) that a further method of calculation produces a result in excellent agreement with experiment, and (ii) that measurements made in the light of the findings discussed earlier in this paper prove that the decay in the gas phase is a ternary reaction.

(i) It is required to calculate the mean life of the atoms, assuming that they can combine only through the medium of a triple collision involving two atoms and one molecule. Let  $\lambda_1$  be the mean free path of the atoms among themselves, and  $\lambda_2$  that of the molecules; further, let  $\bar{u}$  be the r.m.s. velocity of the molecules, then  $\bar{u}\sqrt{2}$  is that of the atoms. Now consider a particular atom  $a_1$ ; it will collide  $\bar{u}\sqrt{2}/\lambda_1$  times per sec. with a similar atom. If a molecule B converts one such atomic impact (between  $a_1$  and  $a_2$ ) into a triple collision at a point L, it must have travelled from a point distant between  $(\lambda_2 - \frac{1}{2}\bar{u}\tau)$  and  $(\lambda_2 + \frac{1}{2}\bar{u}\tau)$  from L,  $\tau$  being the "duration" of the  $a_1$ - $a_2$  collision. Hence, at a time  $t = \lambda_2/\bar{u}$  before the impact, the necessary B molecule must lie in a spherical shell of centre L, of mean radius  $\lambda_2$ , and of thickness  $\bar{u}\tau$  (assumed small compared with  $\lambda_2$ ). The probable number of B molecules in this shell is

$$v_B \cdot 4\pi\lambda_2^2\bar{u}\tau. \quad (1)$$

where  $v_B$  is the concentration of B molecules per c.c. In order, however, that the  $a_1$ - $a_2$ -B impact shall occur, B must be definitely aligned with regard to the colliding atoms, and the collision can follow only if B starts on its journey towards them in a solid angle  $\pi\sigma^2/\lambda_2^2$ , where  $\sigma$  is the radius of the  $a_1$ - $a_2$  complex. The probability that it will travel in this direction is

$$(\pi\sigma^2/\lambda_2^2)(1/4\pi) = \sigma^2/4\lambda_2^2 \quad (2)$$

and the probable number of B molecules present and moving in the right direction is given by the product of (1) and (2), i.e.,

$$[B] = v_B \cdot \pi\bar{u}\tau\sigma^2 \quad (3)$$

The number of such collisions per sec. which the atom  $a_1$  could make (if it were not demobilised by the collision \*) is then given by the product of (3) and the number of atomic collisions, *i.e.*,

$$Z = \pi v_B \bar{u} \tau \sigma^2 \times \bar{u} \sqrt{2} / \lambda_1 = \pi \sqrt{2} \bar{u}^2 \tau \sigma^2 v_B / \lambda_1 \quad . \quad . \quad (4)$$

For nitrogen at 10 mm. pressure and containing 1% of the active form, we have  $\lambda_1 = 8.8 \times 10^{-1}$  cm.,  $v_B = 3.6 \times 10^{17}$ ,  $\bar{u} = 5.0 \times 10^4$  cm./sec., and  $\sigma = 1.9 \times 10^{-8}$  cm.; hence, taking  $\tau$  as  $10^{-14}$  sec., we have  $Z = 1.64 \times 10^{-2}$ , whence the mean free life of an atom, and thus the duration of the after-glow, will be  $1/1.64 \times 10^{-2} = 61$  secs. This is rather longer than that actually observed (7–10 secs.), but in view of the uncertainty as to the numerical values of both  $\tau$  and  $\sigma$  (since the  $a_1$ - $a_2$  complex will probably be an excited molecule, and hence of abnormal diameter), the agreement between calculation and experiment is very good.

A ternary reaction being assumed to give rise to the glow, the intensity,  $I$ , will at any instant be proportional to the rate at which the atoms are combining, *i.e.*, to the number of triple collisions per c.c. per sec.; hence

$$k_1 I = -\partial v_a / \partial t = k_2 v_a^2 v_B$$

Integration gives  $1/v_a = (t + C)k_2 v_B$ ,  $C$  being a constant, but since  $I = k_2 v_a^2 v_B / k_1$ , we have

$$1/\sqrt{I} = \sqrt{k_1 k_2} (t + C) \sqrt{v_B}$$

and hence the slope of the line giving the relation between  $1/\sqrt{I}$  and  $t$  should vary as  $\sqrt{v_B}$ , *i.e.*, as the square root of the total gas pressure,  $P$ .

(ii) Previous attempts (Part V, *loc. cit.*) to examine this point experimentally led to scattered results which showed that the slope varied as  $P$  and not as  $\sqrt{P}$ , but the dependence of the decay rate upon the purity of the gas, and hence upon wall conditions, according to the results described earlier in the present communication, gave the clue to the source of the disagreement between theory and observation, and clearly indicated that the desired correlation should be carried out either (a) by using a gas rich in photogens or (b) in a purer gas but at higher over-all pressures.

Glowing nitrogen containing 0.03% of oxygen was streamed through the observation tube and its decay rate was measured as usual. In order to avoid the introduction of any corrections for changed flow-speed a constant flow of 1600 c.c./hr. at atmospheric pressure was maintained, and the pressure in the apparatus was

\* This does not vitiate the argument, since we are concerned with a statistical discussion of the probable life of the atom.

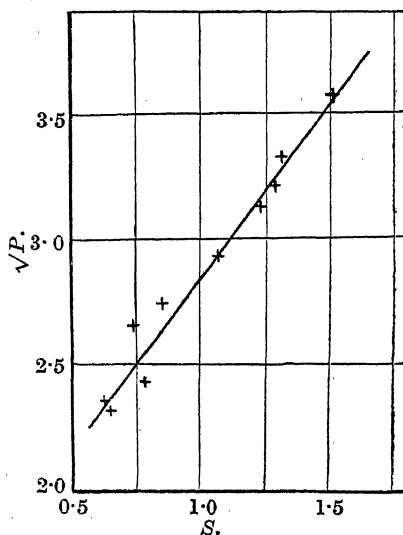
varied by a choking tap in the exhaust line. Fig. 5 shows that the slope ( $S$ ) is a linear function of  $\sqrt{P}$  between 5.4 and 12.8 mm., and that the decay of the glow may therefore be expressed as a third-order process, in agreement with theory.

(c) *The action of oxygen upon the after-glow.* It has been found that when about 5% or more of oxygen is fed to the glow stream and the yellow luminosity is destroyed, the photo-cells behave as if strongly illuminated, although the gases have apparently become dark at the point of observation just below the oxygen inlet. This can only mean that the glow emission is proceeding in the non-visible portions of the spectrum, and as the cells have been found to be practically insensitive beyond the orange region but slightly more so in the green and blue, it follows that a very large radiation in the blue region and beyond must be proceeding in these circumstances. The author is indebted to Mr. G. C. Eltenton for the information that he too has observed this phenomenon (see also Rayleigh, J., 1918, 113, 200).

(d) *Constancy of decay order with time.* Since, except under conditions which can be attributed to wall influence (e.g., Fig. 3), no change in form of the decay curves is found with time, it follows that the mechanism of the process does not alter, at any rate at these pressures, and that between about 5900 and 4000 Å.U. (the sensitivity limits of the photo-cells) the emission takes place regularly among the various bands concerned. This is probably not in disagreement with König and Klinkmann (*Z. physikal. Chem.*, 1928, 137, 335), since the range of curve-lengths over which they worked is much greater than here: the present measurements apply practically only to the  $\alpha$ -bands.

(e) *Photogens and chemical activity in nitrogen.* It has been found that the addition of photo-gas to "pure" nitrogen causes a large increase in the concentration of the chemically active species, this being determined by the reaction with nitric oxide as described in Part IV. Attempts to establish the relationship between glow

FIG. 5.



intensity and concentration of active nitrogen have not yet led to results which can be treated quantitatively, but it appears, in agreement with Bonhoeffer and Kaminsky (*Z. Elektrochem.*, 1926, **32**, 536) and König and Klinkmann (*loc. cit.*), that there is no simple expression which connects them; the former generally tends to rise more rapidly, as is shown in a typical experiment in which the brightness of the glow changed from 0.3 to 3.45, as measured at the point where the analysis was made by the galvanometer deflexion, whilst the concentration increased from 0.44 to 1.40%. The intensity of the green flame produced during the reaction between glowing active nitrogen and nitric oxide appears to bear much the same relation towards the concentration of active species as does the nitrogen glow alone under the same conditions, the supply of nitric oxide being replaced by an equal one of nitrogen to hold the pressure constant. The experiments do, however, show that the same amount of chemically active nitrogen may be present in glows which decay at widely different rates, a point to be discussed later.

(f) *The nature of photogens.* In agreement with Rayleigh (*Proc. Roy. Soc.*, 1915, *A*, **91**, 303) and with Bonhoeffer and Kaminsky (*Z. Elektrochem.*, 1926, **32**, 536), it has been found that the optimum supplies of these gaseous impurities correspond to about 0.1% concentration in the nitrogen, and that water vapour is to be placed very high in the order of effectiveness (compare Herzberg, *loc. cit.*; Lewis, *J. Amer. Chem. Soc.*, 1929, **51**, 654, 665). It has not been found possible to trace any effects of the photogens which can be ascribed to their specific natures, and hence it appears that their action is general in character.

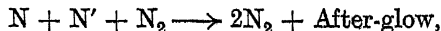
#### *Discussion.*

These experiments appear definitely to clarify the state of our knowledge of active nitrogen. The existence of wall effect now demonstrated is in complete harmony with the results of Lewis and of Herzberg (published during the course of the present research). Among the phenomena to be anticipated from these researches are the reversal of the pressure and temperature effects normally found for the after-glow, and actually observed by Lewis, and also the divergences in the order of the decay process as observed by Kneser and the present author, the cause of this clearly being slight differences in composition of the nitrogen employed and in the surface of the vessels.

More important, however, is the strong evidence for the triple-collision hypothesis and consequent deductions as to the origin of the chemical activity and the close connexion apparently existing between this and the luminosity. It has already been shown, both

in this and in earlier papers, that the ternary-reaction theory leads to the assumption that the glow-producing and chemically active species are present in comparable concentrations, and Kaplan and Cario (*Nature*, 1929, **121**, 906) and Compton and Boyce (*Physical Rev.*, 1929, **33**, 145) have recently shown that active nitrogen contains two species of metastable atoms (2.3 and 3.6 volts) and a metastable molecule (8.2 volts), evidence thus being forthcoming for a substance whose energy agrees well with the value 2.0—2.2 volts (equivalent to 46,000—50,000 cal./g.-mol.) advanced in earlier papers of this series (Parts I, II, and III; J., 1926, 1804; 1927, 669, 2188) for the energy of active nitrogen as it appears in its chemical reactions. Upon these spectroscopic findings, Kaplan and Cario base a theory of the origin of the after-glow. Its emission may result from one or more of three reactions, viz.: (i) recombination of one neutral and one 2.3-volt atom; (ii) recombination of two neutral atoms, followed by excitation of the metastable molecule thus produced by collision with a 2.3-volt atom; (iii) collisional excitation of an 8.2 volt metastable molecule by a 3.6-volt atom: since the latest work (e.g., Gaviola, *Nature*, 1928, **122**, 313) shows that the heat of dissociation of  $N_2 \longrightarrow 2N$  is ca. 9.5 volts, the 11—11.5 volts necessary for emission of the  $\alpha$ -bands by the molecule are provided.

Frl. Sponer (*Z. Physik*, 1925, **34**, 622) has concluded that the emission of the  $\alpha$ -bands (the visible after-glow) follows the recombination of atoms in triple collision with a molecule, the energy of association being transferred to the third body, which is thus excited and re-emits the energy as radiation; as, at the time of her publication, the heat of dissociation of  $N_2 \longrightarrow 2N$  was regarded as 11.4 volts, no collisional excitation was deemed necessary. It seems not unreasonable that the glow emission may be represented by a combination of the Kaplan-Cario and Sponer theories, and that the process is



where  $N'$  is the 2.3-volt metastable atom, assumed to be the chemically active form.\* The right-hand side of this reaction must be regarded as a mere outline, but the left carries with it certain implications which may be considered.

1. It accounts for the third-order decay of the after-glow, and hence for the negative temperature coefficient of this reaction.

2. It is in conformity with the calculations made by the present author as to the comparable concentration of glow-producing and of chemically active species.

\* The findings discussed in sections (a) and (b) (p. 340) suggest also that the walls may under appropriate conditions act as the third body in the reaction.

3. If the analogy with active hydrogen is valid, the existence of strong wall effects may be attributed to adsorption and heterogeneous recombination of nitrogen atoms. Moreover, if we are prepared to admit preferential adsorption of N rather than of N' unless the surfaces are exceedingly "clean," it follows that the glow intensity and decay rates of an active nitrogen stream may be almost infinitely variable without corresponding changes in chemical activity, in agreement with the findings discussed in Part IV of this series and in sections ( $\alpha$ ) and ( $\beta$ ) (p. 340). Since a metastable atom or molecule can undergo many collisions without suffering deactivation—of which a good proportion must be upon the walls—whereas the case of atomic hydrogen shows that for normal atoms the surface influence is very great indeed, this assumption does not appear unjustifiable.

4. It links up glow effects and chemical activity and provides for an entity of the energy content which earlier work has postulated, *viz.*, the metastable atom of about 2.3 volts energy (53,000 cal./g.-mol.) (see p. 347).

There are, however, other possibilities to be considered. The principal objection to this view is that it accounts for only about one-sixth of the total energy available, and does not provide any clue as to why the other excited and metastable species present are apparently chemically inert. On the other hand, it is significant that in the majority of gaseous reactions the energy exchanges involved are much less than the 200,000 cal./g.-mol. with which we are here concerned, and it is possible that too abundant a supply of energy may be unfavourable to chemical changes in general.

Moreover, the Kaplan-Cario theory does not provide for a three-body recombination process, as found definitely in these experiments and less definitely by Kneser. The existence of the strong wall effects noted in this work suggests that it is just possible, although improbable, that the adsorption of the nitrogen varies as the pressure, leaving less free surface for the wall action and, by thus favouring the homogeneous decay, leading to an erroneous inference as to the effect of pressure upon the glow transformation process.

#### *Summary.*

1. The decay of the nitrogen after-glow has been restudied with an improved technique, and found to be most probably partly homogeneous and partly heterogeneous, according to experimental conditions.

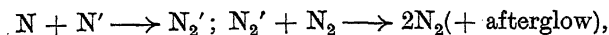
2. Unless the walls of the vessels concerned are "poisoned" by foreign gases, the recombination process is non-luminous and occurs as a surface reaction; as the concentration of the impurity rises,



the wall reaction diminishes and the homogeneous decay increases, but above a limit of *ca.* 0.1% the impurity reacts chemically with the active nitrogen and interferes with the normal decay.

3. The order of the decay process is determined by the state of the walls, which in turn depends upon the purity of the nitrogen employed; when the surface reaction is minimised, the effects of pressure and addition of other gases are in agreement with the three-body recombination theory.

4. The after-glow probably originates in a reaction



$N'$  being a 2.3-volt metastable atom which is the chemically active species whose energy has been measured earlier.

5. No changes are to be seen in the order of the decay as it proceeds; neither do the spectral characteristics of the glow between *ca.* 5900 and 4000 Å.U. appear to alter.

The author's thanks are due to Major F. A. Freeth, F.R.S., and to Professor F. G. Donnan, F.R.S., for providing facilities for the prosecution of these researches, which were carried out in 1928 and the early part of 1929. The co-operation of his assistant, Mr. W. A. Bayliss, has been invaluable.

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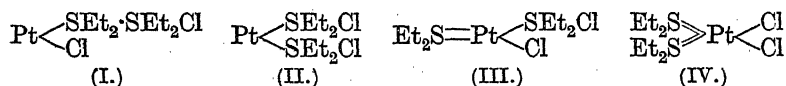
[Received, October 21st, 1929.]

## L.—*A New Interpretation of the Isomerism amongst Co-ordination Compounds of Platinum.*

By FREDERICK GEORGE ANGELL, HARRY DUGALD KEITH DREW,  
and WILLIAM WARDLAW.

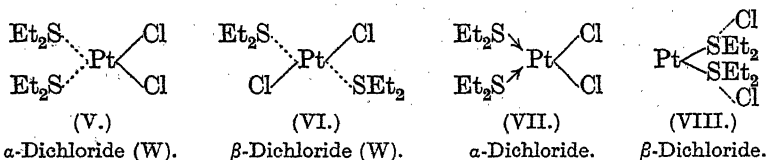
THE apparently well-established *cis*- and *trans*-isomerism found among compounds of quadricovalent platinum provides the strongest remaining evidence for the view that the four groups surrounding a central atom may be situated in a plane instead of at the corners of a tetrahedron. We are engaged in a re-examination of the cases in which isomerism of this kind is alleged, and the present paper is concerned with the compounds which platinous chloride forms with diethyl sulphide, these substances being typical of a group in which the evidence for a planar configuration seems most complete. We have now concluded, however, that the isomerism in this instance is of a structural and not of a spatial nature, and hence that, so far as these particular substances are concerned, there is no reason to doubt that the space distribution of four groupings associated with platinum is tetrahedral.

Blomstrand (*J. pr. Chem.*, 1888, **38**, 352) found that diethyl sulphide united with platinous chloride, giving two distinct dichlorides to which he assigned the structures (I) and (II), regarding



$\alpha$ -Dichloride (B).  $\beta$ -Dichloride (B).  $\alpha$ -Dichloride (K).  $\beta$ -Dichloride (K).

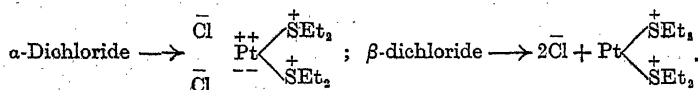
both substances as containing bivalent platinum. Klason (*Ber.*, 1895, **28**, 1493) extended these observations, and gave the new formulæ (III) and (IV), where platinum is quadrivalent, or perhaps sexavalent in the  $\beta$ -compound. Neither author contemplated a planar configuration, or gave really satisfactory proof of the structures he alleged, although useful and mainly accurate data were accumulated. Werner ("Lehrbuch der Stereochemie," pp. 338 *et seq.*; see also *Z. anorg. Chem.*, 1893, **3**, 310), ignoring the relevant chemical evidence of his predecessors, attributed the isomerism to the presence of *cis*- and *trans*-planar types, (V) and (VI), in which



platinum exhibited 4-co-ordination. His view is universally accepted at the present time, although Reihlen has consistently adhered to an hypothesis of the tetrahedral distribution of valencies (*Annalen*, 1927, **447**, 211; **448**, 1312; *Z. anorg. Chem.*, 1926, **151**, 71).

The structures which we propose as a result of the present work are shown in (VII) and (VIII). In the  $\alpha$ -dichloride each sulphur atom is united to tetrahedral platinum by a co-ordinate link \*

\* After this paper had been read, Dr. N. V. Sidgwick pointed out to us that dissociation of the  $\alpha$ - and  $\beta$ -dihalides would give rise to the *same* ions in both cases, if the co-ordinate links between the sulphur atoms and the platinum atom in the  $\alpha$ -compound were equivalent to semipolar double bonds:



With this proviso, therefore, the  $\alpha$ - and  $\beta$ -forms are inter-related in a manner close and unprecedented. The un-ionised forms are nevertheless not identical, because the halogen atoms are situated in different positions in the molecule in the two cases; nor do the two substances represent the ionised and un-ionised forms of the same substance, because the chemical evidence shows, to take one point of several which could be cited, that the  $\beta$ -dichloride is ionised

constituted by the sharing with platinum of two electrons derived from each sulphur atom; whilst in the  $\beta$ -dichloride the linkings between the sulphur atoms and platinum are covalencies and the chlorine atoms are potentially ionised as in the sulphonium halides.

Blomstrand and Klason observed that, whilst both the  $\alpha$ - and the  $\beta$ -dichloride had the normal molecular weight, the yellow colour of the  $\alpha$ -compound was deeper than that of the  $\beta$ -, and in addition the former substance was the more soluble in organic solvents. The  $\beta$ -compound alone showed noticeable solubility in water, and, more significant, it reacted much more rapidly with alcoholic silver nitrate. The conductivity of both dichlorides in aqueous alcohol was very low; but that of the  $\beta$ -isomeride was distinctly the higher. The  $\alpha$ - was transformed to the  $\beta$ -dichloride by treatment with hot aqueous diethyl sulphide. The reverse change could be effected by conversion, through silver sulphate and potassium bromide, or through the latter alone, into the dibromide, which with silver chloride gave the  $\alpha$ -dichloride. The dibromide and di-iodide existed in one form only, and this form was stated by Blomstrand to be a  $\beta$ -form and by Klason an  $\alpha$ -form.

By slight modification of the original procedure, we have been able to prepare at will either the  $\alpha$ - or the  $\beta$ -dichloride from diethyl sulphide and potassium chloroplatinite, the latter being best prepared from chloroplatinic acid and potassium oxalate. The  $\alpha$ -dichloride is readily purified by taking advantage of its solubility in light petroleum, and the  $\beta$ -dichloride by making use of the fact that it separates from benzene as a sparingly soluble crystalline

to the extent of about 50% in aqueous solution and yet exists therein free from the  $\alpha$ -form, although we should expect rapid recombination of the ions to produce the insoluble  $\alpha$ -form, which would be precipitated.

In our opinion, the crux of the matter lies in the assumption that the co-ordinate linkings in the  $\alpha$ -compound are equivalent to semipolar double bonds. This assumption cannot be true, because it contradicts the experimental evidence. We are left with only two reasonable alternatives, *viz.*, (1) that the co-ordinate link is an ordinary double bond consisting of two covalencies, which means that the normal shells for the sulphur atoms are expanded in the  $\alpha$ -compounds, the sulphur atom being quadricovalent; or (2) that the co-ordinate links in the  $\alpha$ -compounds are formed by the sharing with platinum of two electrons from each sulphur atom, the sharing not being such as to provide a free unit charge on the platinum atom for each co-ordinate link. The extent to which such sharing takes place cannot at present be assessed in any particular case; and it will depend in the general case on the nature of the two atoms concerned (compare *J. Soc. Chem. Ind.*, 1928, 47, 949). At present we refrain from deciding between these two possibilities. It may be that both types of bonding will be found among co-ordinately linked atoms; but we are inclined to prefer the second possibility in the case of the substances under consideration.

compound with a molecule of the solvent. We have confirmed the molecular weights and analyses of the two substances, and also their physical properties as given by Klason. The most noticeable physical differences between the isomerides, apart from the colours, lie in their solubilities, those of the  $\alpha$ -dichloride suggesting a non-polar compound whereas those of the  $\beta$ -dichloride indicate a weakly polar substance. The  $\beta$ -dichloride was sufficiently soluble in water for its conductivity to be measured, and the values obtained showed that the salt is considerably ionised—about 50% at  $v = 1000$  if  $\mu_{\infty}$  be taken as 100.

We find that the chemical properties of the two dichlorides are so different as to render it highly improbable that they are merely spatial isomerides. The ready transformation, under certain conditions, of the  $\beta$ -compounds to the  $\alpha$ - seems to have been the main cause which in the past has prevented a recognition of their true relationship. We have, for example, been able to isolate a second dibromide and to show that this is a  $\beta$ -compound, which, when melted at  $95^{\circ}$ , passes almost completely into the  $\alpha$ -isomeride, m. p.  $129^{\circ}$ ; and we have obtained evidence that a  $\beta$ -di-iodide exists and is still more easily converted into the  $\alpha$ -di-iodide.

On being kept in the solid state, or in solution or suspension in alcohol or benzene, either dichloride tends to pass into an equilibrium mixture of both. The isomeric dibromides change in a similar manner but much more rapidly; but here the equilibrium mixture consists almost entirely of the  $\alpha$ -compound. The di-iodides tend even more strongly to attain the  $\alpha$ -state. In carrying out reactions, therefore, it has been found necessary to work with freshly prepared or freshly tested substances and to effect the rapid isolation and examination of the products. In some cases, as will be seen later, the influence of solvents becomes important, and the effect of temperature must also be taken into account.

The most striking chemical difference between the members of the two series of isomeric dihalides, however, is shown by their interaction with silver oxide in presence of water. The  $\beta$ -dichloride, for example, reacts in a few minutes with the production of silver chloride and a markedly basic substance, *platinumbisdiethylsulphonium hydroxide* (IX), which is readily soluble in water. This substance, which may be referred to as the  $\beta$ -base, can be obtained in transparent, yellowish, deliquescent crystals which rapidly absorb carbon dioxide when exposed to the air. After being dried over phosphoric oxide, the base gives correct analytical figures for a dihydroxide. Its aqueous solution is strongly alkaline to litmus, has a moderate conductivity, precipitates metallic hydroxides, and neutralises acids, both mineral and organic, with the production of

pure  $\beta$ -salts provided that the temperature is below the point of their transformation to the  $\alpha$ -compounds.



In this manner, besides the  $\beta$ -dichloride, the  $\beta$ -dibromide and the  $\beta$ -oxalate (X) were prepared, and were shown to belong to the  $\beta$ -series by quantitative reconversion into the  $\beta$ -dichloride, the former by means of silver oxide and hydrochloric acid, and the latter by means of the acid alone. The oxalate, a colourless substance readily soluble in water and in benzene, reacts at once with lime-water, giving a precipitate of calcium oxalate and a solution of the pure  $\beta$ -base, a reaction which suggests ionisation of the oxalate in aqueous solution. Determination of the conductivity confirmed this.

When an aqueous solution of the base was gradually neutralised with 0.5*N*-hydrochloric acid, the  $\beta$ -dichloride initially precipitated rapidly redissolved, but the precipitate became permanent before the half-neutralisation stage was reached. At this stage 0.12 g. of pure  $\beta$ -dichloride had been precipitated from a measured volume of solution which, as shown by another experiment, would have given on full neutralisation a precipitate of 0.54 g. of  $\beta$ -dichloride. Thus, at half-neutralisation the alkaline filtrate from  $\beta$ -dichloride still contains that substance, together with the free base and possibly a proportion of hydroxychloride. On evaporation at the ordinary temperature, this filtrate gave a yellow alkaline oil which partly solidified in a paste. This experiment shows that the  $\beta$ -base is not a complex substance like the base derived from the  $\beta$ -series of Vernon's dimethyltelluronium dihalides.

The  $\alpha$ -dichloride, on the other hand, is only very slowly changed by moist silver oxide under precisely similar conditions, the reaction being incomplete after 48 hours. The evolution of diethyl sulphide commences at once, and the formation of silver chloride is attended by the precipitation of platinum as oxide or hydroxide. The filtrate is quite neutral to litmus:  $\text{Pt}(\text{Et}_2\text{S})_2\text{Cl}_2 + \text{Ag}_2\text{O} = 2\text{Et}_2\text{S} + 2\text{AgCl} + \text{PtO}$ . The same distinction holds good for the isomeric dibromides and di-iodides.

These experimental results cannot be explained adequately on Werner's formulæ. The fundamental difference between the  $\alpha$ - and the  $\beta$ -dichloride in their behaviour with silver oxide demonstrates most clearly that the isomerism is structural. On the new formulæ which we propose, the experimental results find a natural interpretation. The  $\alpha$ -dichloride should give wholly silver chloride and the unstable co-ordination compound  $(\text{Et}_2\text{S})_2\text{Pt}(\text{OH})_2$ , which would be expected to decompose into diethyl sulphide and platinum

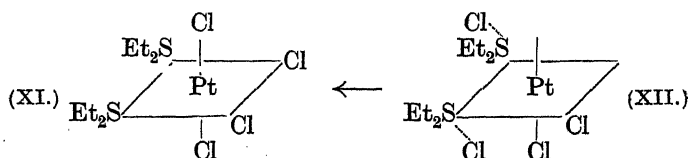
oxide or hydroxide. The  $\beta$ -dichloride, on the other hand, should furnish silver chloride and the stable base (IX). Both the  $\beta$ -dichloride and the base should be ionised in aqueous solution. Each of these deductions has received confirmation. The reason why the  $\beta$ -dichloride is less polar in character than a true alkylsulphonium halide may well be that the influence of the bivalent platinum atom, which has clearly a tendency to attract electrons, prevents, by restraining to some extent the valency electrons possessed by the sulphur atom, the full development of ionisation of chlorine in the  $\beta$ -dichloride, since this development can occur only if the sulphur atoms are able to yield to the chlorine atoms their fourth valency electrons. The chlorine atoms are therefore partly covalent in the  $\beta$ -dichloride; nevertheless, in aqueous solution it exhibits appreciable conductivity. The  $\alpha$ -dichloride is completely non-polar because the chlorine atoms are attached to platinum by covalencies.

The only other example of the production of a basic substance from a platinum compound of this type is described by Blomstrand (*loc. cit.*, p. 362), who noticed that the sulphate derived from a dichloride of the dimethyl sulphide series gave an alkaline filtrate when sulphuric acid was removed by the action of baryta. The liquid left, on spontaneous evaporation, a brownish semi-solid residue, but Blomstrand states that the substance could not be obtained in a condition suitable for analysis. Imagining that the hydroxyl groups were attached to platinum, he gave the formula  $\text{Me}_2\text{S} \gg \text{Pt} \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$ , although he considered that the sulphate belonged to the  $\alpha$ -series. Owing, probably, to the gummy nature of his product, Blomstrand failed to follow up his observation by investigating the action of acids upon this substance, contenting himself with the remark that the base absorbed carbon dioxide.

Blomstrand found that either the  $\alpha$ - or the  $\beta$ -dichloride, when treated with aqueous silver sulphate and filtered, gave a solution of a sulphate which yielded a dibromide (m. p.  $118^\circ$ ) on treatment with potassium bromide. Klason, who gives m. p.  $124^\circ$ , states that this is an  $\alpha$ -dibromide and that the same substance is produced by the interaction of alcoholic potassium bromide with either dichloride. We now find that the interaction of the  $\beta$ -dichloride with silver sulphate and potassium bromide in the cold gives the pure  $\beta$ -dibromide (m. p.  $95^\circ$ ), identical with that produced by the interaction of the  $\beta$ -dichloride and alcoholic potassium bromide, and also with that prepared by neutralising the  $\beta$ -base with hydrobromic acid. The  $\alpha$ -dichloride does not interact either with alcoholic potassium bromide or with aqueous silver sulphate at the ordinary temperature; if, however, the latter mixture is boiled, some diethyl sulphide is

evolved (probably from the unstable  $\alpha$ -sulphate), and the aqueous diethyl sulphide then converts the remaining  $\alpha$ -dichloride into the  $\beta$ -isomeride, which interacts with the production of  $\beta$ -sulphate. It is evident, therefore, that Blomstrand and Klason must have heated the reaction mixture containing  $\alpha$ -dichloride, thereby producing  $\beta$ -dichloride, and also that they must at some stage have heated to at least  $95^\circ$  the  $\beta$ -dibromide prepared from the  $\beta$ -dichloride, thereby converting it into the  $\alpha$ -dibromide. These puzzling differences of opinion are therefore to be referred to the occurrence of inter-transformation between members of the  $\alpha$ - and the  $\beta$ -series.

Further convincing evidence in favour of our structures for the  $\alpha$ - and  $\beta$ -compounds has been obtained by the following methods. When chlorine is added to either of the isomeric dichlorides, conversion into the tetrachloride occurs. Our formulæ indicate that the  $\alpha$ -dichloride should give rise to the octahedral form (XI), whereas the  $\beta$ -dichloride should yield the tetrahedral form (XII). We should expect these compounds to differ in properties as profoundly as do the isomeric dihalides. Moreover, (XII) should become transformed to (XI) by means similar to those which effect the change  $\beta$ -dihalide  $\rightarrow$   $\alpha$ -dihalide.

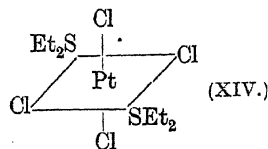
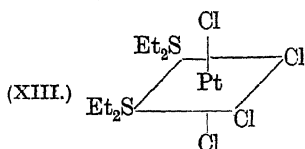


Blomstrand states that no isomerism exists amongst the tetrahalides. He prepared the same yellow tetrachloride (m. p.  $175^\circ$ ) by the addition of chlorine to either dichloride, and he obtained similar results with the tetrabromides, tetraiodides, and a series of tetrahalides containing mixed halogens. We find, however, that the  $\alpha$ -dichloride gives rise quantitatively to a yellow crystalline  $\alpha$ -tetrachloride (XI), m. p.  $198^\circ$ , whilst the  $\beta$ -dichloride gives, also quantitatively, a paler yellow crystalline  $\beta$ -tetrachloride (XII), which melts at  $133^\circ$  and immediately resolidifies, forming the  $\alpha$ -tetrachloride (XI). The  $\beta$ -tetrachloride is transformed to the  $\alpha$ -isomeride on being boiled for a few minutes in ethyl or methyl alcohol, although by very rapid crystallisation it may be obtained unchanged from solution in the former solvent. Like the  $\alpha$ -tetrachloride, however, it is unaltered by crystallisation from hot benzene, a non-ionising solvent. The transformation of the  $\beta$ - to the  $\alpha$ -tetrachloride is therefore an ionic reaction which can be brought about by raising the temperature or by the use of a polarising solvent; and this is precisely what could be predicted from inspection of the formulæ (XII) and (XI).

The  $\alpha$ - and  $\beta$ -tetrabromides were prepared in an analogous manner. They are similarly inter-related, but the transformation of the  $\beta$ - to the  $\alpha$ -form is even more readily effected than it is among the tetrachlorides.

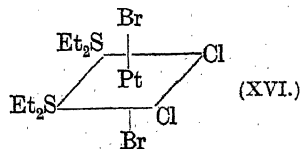
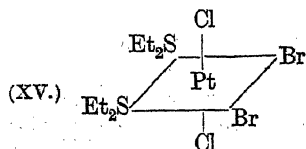
When the  $\beta$ -tetrahalides are kept in the solid state their melting points tend to rise, whilst those of the  $\alpha$ -tetrahalides appear to fall slightly. It would seem, therefore, that close parallelism exists among the  $\alpha$ - and  $\beta$ -dihalides and the corresponding tetrahalides, dynamic equilibria being set up in both cases. The  $\alpha$ -tetrahalides may be regarded as bis-dipolar compounds in which each platinum atom bears a double negative charge, whilst the sulphur atoms are each positively charged, this picture giving complete analogy with the accepted formulation of chloroplatinic acid except that the positively charged atoms are in that case free instead of being bound to the platinum atom by covalencies. Alternatively, the  $\alpha$ -tetrahalides may be regarded as containing each two co-ordination linkings between platinum and the sulphur atoms, as in the  $\alpha$ -dihalides.

It may be urged that the planar formulæ of Werner also account satisfactorily for the existence of two tetrachlorides, which would necessarily have the formulæ (XIII) and (XIV). Although we



considered that these formulæ, which might well represent difficultly interchangeable forms, could not account for the experimental results as convincingly as did (XI) and (XII), yet further evidence seemed necessary to prove finally the inadequacy of Werner's supposition. This was obtained from the results of an investigation of the dichlorodibromides.

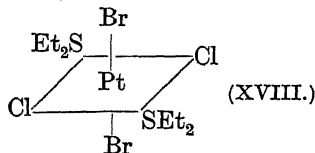
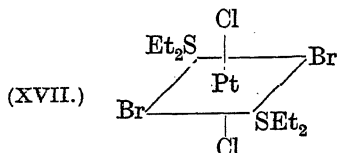
On the planar hypothesis, if no spontaneous rearrangements of valencies occur, by adding chlorine to the  $\alpha$ -dibromide a dichlorodibromide (XV) should be produced which should differ from that



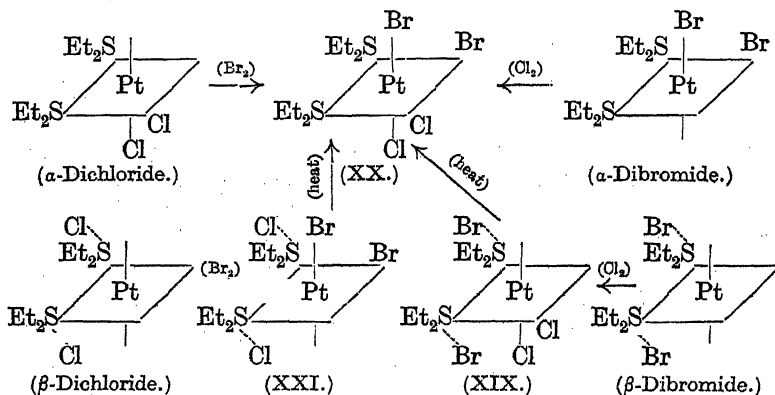
(XVI) obtained on adding bromine to the  $\alpha$ -dichloride. On our hypothesis, however, the two substances should be identical; and we find that this is indeed the case, the sole product being (XX).



As products of the corresponding changes in the  $\beta$ -series, the planar hypothesis demands, respectively, the two substances (XVII)



and (XVIII), which should be identical, but different from either (XV) or (XVI). We find that neither of these demands is satisfied.\* Labile tetrahedral forms, (XIX) and (XXI), are in both cases initially produced, which may readily be caused to change into the octahedral form (XX), and this is identical with the dichlorodibromide from the two  $\alpha$ -dihalides. There is thus, finally, only one dichlorodibromide from the four sources, and the order in which the two different halogens are added is immaterial. The labile forms (XIX) and (XXI) are different, although closely similar, substances, whose properties show that they belong to the  $\beta$ -tetrahalide series; whilst (XX) is, of course, an  $\alpha$ -tetrahalide.

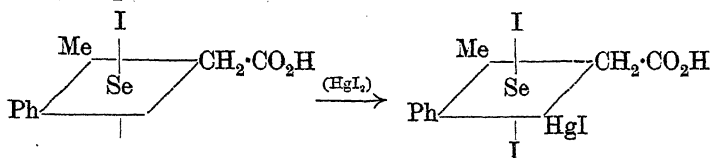


A curious distinction was noticed between the  $\alpha$ - and  $\beta$ -compounds of both the di- and the tetra-halide series: the  $\alpha$ -compounds are without exception "electrified" when rubbed upon glass with a bone spatula, the particles scattering strongly when detached from the glass in the attempt to collect them; but the pure  $\beta$ -compounds, dried under the same conditions, do not become "charged." A small proportion of  $\alpha$ -compound present as impurity in a  $\beta$ -compound may be detected in this manner. We are not aware that this

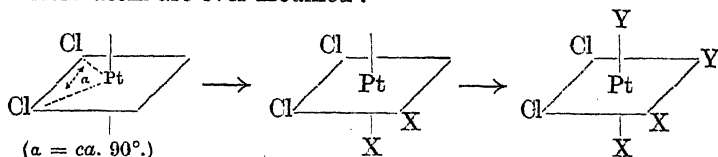
\* Even if we suppose that Werner's configurations should be reversed, the  $\alpha$ -compounds being *trans*- and the  $\beta$ -compounds *cis*-planar forms, anomaly still persists.

phenomenon has been noticed before in connexion with isomeric series. The triboelectric character of the  $\alpha$ -compounds is presumably to be ascribed to asymmetry of crystalline structure.

The conclusion emerges from our experiments that virtually quadrivalent platinum in this series is of tetrahedral space structure, and that, when this is converted into the octahedral form, the two entering groups take up exclusively *cis*-positions. In other words, the octahedron is a simple derivative of the tetrahedron, without rearrangement of groupings, the six valency electrons of platinum having directions which are approximately fixed in space. This conclusion is entirely in accord with the results of Pope and Neville (J., 1902, 81, 1552) in connexion with octahedral sulphur and selenium. They find, for example, that, when mercuric iodide is added to optically active phenylmethylselenitine iodide, complete racemisation is produced, showing that the groups HgI and I must take up *cis*-positions:



The present experiments show, further, that tetrahedral platinum must be regarded as derived from the planar bivalent form by the similar *cis*-addition of groups, whence it follows that the valencies of platinum in platinous chloride are inclined at an angle of some  $90^\circ$ . It is improbable, therefore, that in passing from bivalent to quadrivalent (or quadricovalent) and to octahedral platinum the entering groups take up at either stage other than neighbouring positions of the developed octahedron; and it becomes unnecessary to suppose that the directions in space of the six valencies around the platinum atom are ever modified:



There is thus a possibility that the skew tetrahedron representing, *e.g.*, an  $\alpha$ -dihalide may be sufficiently permanent to confer molecular asymmetry. This aspect is under examination.

If it be accepted that in the  $\beta$ -compounds of this series the halogens are united with sulphur and not with platinum, far-reaching questions are at once raised. The case of the platinamines is so similar to that at present being considered as to suggest that the

structure must be analogous in both, and it would therefore follow that in the true  $\beta$ -series of platinamines the halogen atoms are united with nitrogen and should be capable of replacement by hydroxyl to give strongly basic substances, e.g.,  $\text{Pt} \begin{smallmatrix} \text{NH}_3 \cdot \text{OH} \\ \text{NH}_3 \cdot \text{OH} \end{smallmatrix}$ .

Evidence that a base of this nature can indeed be produced was put forward by Odling many years ago (*Chem. News*, 1870, **21**, 289), but the significance of his experiments appears to have been overlooked. It seems clear that the structures of many other amines must be re-examined in the light of these results, and we are now engaged in work upon the foregoing platinamines and other substances. We intend also to examine the possibility of resolving into optically active components (i) the halides of the  $\beta$ -series of the form  $\text{Pt} \begin{smallmatrix} \text{SRR}'/\text{Hal} \\ \text{SRR}'/\text{Hal} \end{smallmatrix}$ , in which the sulphur atoms should be centres of asymmetry, and (ii) compounds of type (XX), in which the molecule should be asymmetric on our theory but not on that of Werner.

#### EXPERIMENTAL.

*Preparation of the Isomeric Dichlorides.*—Potassium chloroplatinite, dissolved in about 5 times its weight of water, was shaken with a slight excess above 2 mols. of diethyl sulphide. (a) If the  $\alpha$ -dichloride was required, the yellow precipitate, which consisted mainly of this isomeride, was removed after 2 hours, and the  $\alpha$ -dichloride was crystallised from light petroleum (b. p. 40–60°), in which the  $\beta$ -isomeride did not dissolve. The aqueous mother-liquor, after concentration at the ordinary temperature, deposited yellowish-white needles of the  $\beta$ -dichloride. As soon as the aqueous liquid commenced to deposit potassium chloride, it was extracted with chloroform, which removed the remaining isomeric dichlorides. In one instance, pure  $\alpha$ -dichloride was obtained on evaporation of the chloroform extract. (b) If the  $\beta$ -dichloride was required, the yellow precipitate (above) was kept with the mother-liquor in a closed flask for a day, whereupon most of it redissolved. The filtrate from undissolved material (a mixture of the two dichlorides), when evaporated at the ordinary temperature or when freed from ethyl sulphide by passage of air through the liquid, yielded the pure  $\beta$ -dichloride. The residual liquid was finally treated as in (a). The total yield of the two isomerides was almost quantitative.

The  $\alpha$ -dichloride (VII), m. p. 106–108°, is insoluble in water, but readily soluble in ether, chloroform, benzene, and other organic solvents. It separates from light petroleum in bright yellow platelets, and from benzene in large yellow prisms which are without solvent of crystallisation. It crystallises well from alcohol in

prismatic needles (Found: C, 21.55; H, 4.5; Pt, 43.7; *M*, cryoscopic in benzene, 434. Calc. for  $C_8H_{20}Cl_2S_2Pt$ : C, 21.5; H, 4.5; Pt, 43.7%; *M*, 446.5). It reacts rather slowly with silver nitrate in alcoholic solution; after 2 days, the filtrate from silver chloride gives with potassium chloride a mixture of the  $\alpha$ - and the  $\beta$ -dichloride.

The  $\beta$ -dichloride (VIII) melts at 106–107° and is almost white. It is appreciably soluble in water and readily soluble in chloroform. In benzene it first dissolves and then separates in large, light yellow prisms, which often show square faces, containing 1 mol. of benzene of crystallisation which is lost on exposure to the atmosphere or at 60° (Found:  $C_6H_6$ , 14.2. Calc.:  $C_6H_6$ , 14.9%). The  $\beta$ -dichloride is only sparingly soluble in ether or in light petroleum. When melted, it gives after solidification a mixture of the  $\alpha$ - and the  $\beta$ -dichloride (Found, for solvent-free  $\beta$ -dichloride: C, 21.65; H, 4.55; Pt, 43.75; *M*, cryoscopic in benzene, 438).

When the  $\alpha$ - and the  $\beta$ -dichloride are mixed, there is very marked depression of the melting point.

*Interconversion of the Isomeric Dichlorides.*—The  $\alpha$ -dichloride is partly converted into the  $\beta$ -isomeride on being heated either alone or in alcoholic solution, or much more completely by Blomstrand's method of treating it with further aqueous diethyl sulphide, preferably in the warm (Klason), which causes it to enter into colourless solution in proportions so high as to suggest the formation of a new soluble complex with diethyl sulphide stable only in presence of an excess of the sulphide. The  $\beta$ -dichloride is partly converted into the  $\alpha$ -isomeride on being melted or on being allowed to remain in solution in benzene for some weeks. When kept, each of the crystalline dichlorides slowly reverts to a mixture of both.

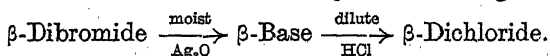
*Action of Moist Silver Oxide on the Isomeric Dichlorides.*—(1) The  $\alpha$ -dichloride, ground in a glass mortar with excess of silver oxide and a little water, was only very slowly changed, with production of free diethyl sulphide, silver chloride, and insoluble platinum oxide or hydroxide. After 48 hours, the filtrate showed no alkalinity to litmus and gave no precipitate with dilute hydrochloric acid except a negligible trace of silver chloride. The precipitate, dried at the ordinary temperature and extracted with benzene, gave some unchanged  $\alpha$ -dichloride. The insoluble residue was shown to contain both silver chloride and platinum oxide or hydroxide.

(2) The  $\beta$ -dichloride reacted rapidly when treated with silver oxide in the same manner, the change being complete in less than  $\frac{1}{2}$  hour. The clear, faintly yellow filtrate from silver oxide and chloride had no odour of diethyl sulphide. It was strongly alkaline to litmus, and when neutralised with dilute hydrochloric acid gave a crystalline precipitate of the pure  $\beta$ -dichloride. The aqueous solution of this

$\beta$ -base, when evaporated to dryness in a vacuum over phosphoric oxide at the ordinary temperature, gave pale yellow hygroscopic crystals of *platinumbisdiethylsulphonium hydroxide* (IX), which, like the aqueous solution, soon absorbed carbon dioxide if exposed to air (Found, in base exposed to air as little as possible : C, 23.85; H, 5.15; Pt, 47.3, 47.75.  $C_8H_{22}O_2S_2Pt$  requires C, 23.45; H, 5.4; Pt, 47.7%). The dried base was easily soluble again in water or in ethyl alcohol. Hydrogen sulphide produced a brown precipitate of a sulphide of platinum, diethyl sulphide being liberated.

By neutralising the aqueous solution of the  $\beta$ -base with aqueous acids, the following salts, shown to be of the  $\beta$ -series by the reactions briefly summarised below, were prepared.

The  $\beta$ -dibromide,  $Pt(SET_2Br)_2$ , separated from alcohol in pale yellow, domed prisms, m. p.  $93-95^\circ$ ; the melt resolidified and then remelted at  $128-129^\circ$ . The substance was identical with a specimen of  $\beta$ -dibromide prepared by a second method, *viz.*, the action of alcoholic potassium bromide in the cold upon the  $\beta$ -dichloride, also dissolved in alcohol; a mixed m. p. of the two specimens showed no depression. A third method, the action (which is rapid) of moist silver sulphate upon the  $\beta$ -dichloride in the cold, followed by filtration and addition of aqueous potassium bromide to the filtrate, gave identically the same substance. The  $\beta$ -dibromide is more soluble in benzene than the corresponding dichloride (Found : Pt, 36.8.  $C_8H_{20}Br_2S_2Pt$  requires Pt, 36.45%). It slowly reverts to the  $\alpha$ -isomeride when kept, and more rapidly when left in contact with alcohol. The structure was checked by the following reactions :



The  $\alpha$ -dibromide,  $PtBr_2(SET_2)_2$ , prepared by heating the  $\beta$ -dibromide at  $100^\circ$  for a few minutes, the transformation being nearly quantitative, crystallised from ethyl alcohol in large, golden-yellow, hexagonal spangles, m. p.  $129^\circ$  (Found : Pt, 36.25%). An alcoholic solution of potassium bromide was without action upon the  $\alpha$ -dichloride : even when the liquid was warmed for a few minutes, the dichloride was recovered unchanged.

The  $\beta$ -oxalate (X) formed colourless transparent crystals when its aqueous solution was allowed to evaporate. It was very soluble in water, the solution being neutral to litmus and giving with lime-water a deposit of calcium oxalate and a solution of the  $\beta$ -base, from which, after filtration, the addition of hydrochloric acid precipitated the pure  $\beta$ -dichloride. The latter is also precipitated by direct addition of hydrochloric acid to a solution of the  $\beta$ -oxalate. The  $\beta$ -oxalate melts near  $60^\circ$  if heated slowly, but the melt is not clear and partial resolidification occurs, the solid melting again near  $95^\circ$ .

Probably partial transformation to an  $\alpha$ -form takes place at the lower temperature. The substance is in part soluble in benzene, separating as an oil which solidifies on standing to a crystalline mass apparently identical with the initial  $\beta$ -oxalate. For analysis it was crystallised from water and dried over phosphoric oxide (Found : C, 25.7; H, 4.4; Pt, 42.25.  $C_{10}H_{20}O_4S_2Pt$  requires C, 25.9; H, 4.35; Pt, 42.1%).

A sulphate crystallising with  $7H_2O$  was prepared by Blomstrand (*loc. cit.*) from either dichloride by treating it with aqueous silver sulphate, and hence he prepared what we now know to be the  $\alpha$ -dibromide, by treatment with potassium bromide. Klason afterwards showed that Blomstrand's  $\alpha$ -dichloride contained 20% of  $\beta$ -dichloride, to which its behaviour (above) is now shown to be due.

Although Blomstrand correctly assigned his sulphate to the  $\beta$ -series, he did so because he prepared from it a dibromide which he thought, incorrectly, to be a  $\beta$ -compound. In reality, he must have obtained the  $\beta$ -dibromide which he unwittingly transformed to the  $\alpha$ -isomeride by heating the solution at some stage. We prepared the  $\beta$ -sulphate,  $Pt \begin{smallmatrix} SEt_2 \\ SEt_2 \end{smallmatrix} SO_4$ , from the  $\beta$ -dichloride with silver sulphate and found (p. 354) that its aqueous solution precipitated the pure  $\beta$ -dibromide on treatment in the cold with aqueous potassium bromide. The same result was obtained when the  $\beta$ -base was neutralised with sulphuric acid, and potassium bromide added to the solution. The sulphate is therefore certainly a  $\beta$ -sulphate. We found, also, that the  $\alpha$ -dichloride was unaffected in the cold by moist silver sulphate after 16 hours. If, however, the mixture was heated at  $100^\circ$  for some minutes, diethyl sulphide was evolved, and this in the presence of water changed some unaltered  $\alpha$ -dichloride to the  $\beta$ -isomeride, which, in turn, reacted with silver sulphate to produce a proportion of  $\beta$ -sulphate. The  $\alpha$ -sulphate, therefore, is probably unstable; and, in any case, it cannot be prepared in this manner.

The  $\beta$ -dichromate, prepared from the  $\beta$ -base with potassium dichromate and sulphuric acid, separated from benzene in dark red needles, m. p.  $140^\circ$ . It was decomposed by hot ethyl alcohol.

*Attempts to prepare the Isomeric Di-iodides.*—Blomstrand prepared a di-iodide (m. p.  $136^\circ$ ) from the sulphate with potassium iodide. He considered this to be a  $\beta$ -compound, but Klason assigned it to the  $\alpha$ -series. The following experiments indicate that the  $\alpha$ -di-iodide melts at  $142$ – $144^\circ$  and that the  $\beta$ -di-iodide changes into it without melting. Attempts to isolate a pure specimen of the  $\beta$ -di-iodide have been fruitless.

(1) Alcoholic potassium iodide reacted in the cold with an alcoholic solution of the  $\alpha$ -dichloride (contrast the behaviour of potassium bromide, p. 361). Orange-red crystals of a di-iodide were obtained, which, after extraction by cold benzene, reddened near  $115^\circ$  and melted at  $141$ – $143^\circ$ . By crystallisation from alcohol, square orange prisms in serrated clusters, m. p.  $142$ – $144^\circ$ , were obtained. This substance gave no  $\beta$ -base with moist silver oxide; the mixture slowly evolved diethyl sulphide. The substance was therefore the  $\alpha$ -di-iodide. When the above reaction mixture is heated, some diethyl sulphide is evolved.

(2) Alcoholic potassium iodide reacted at once in the cold with an alcoholic solution of the  $\beta$ -dichloride, giving a di-iodide (m. p.  $138$ – $140^\circ$ ), which was apparently identical with the former substance. Silver oxide, however, acted upon it to give a very small proportion of  $\beta$ -base.

(3) The action of hydriodic acid (colourless) on a solution of the  $\beta$ -base at the ordinary temperature gave a product (orange-yellow, m. p.  $138$ – $140^\circ$ ), which crystallised from alcohol in the same form, and did not depress the m. p. of the former product. It gave no  $\beta$ -base with moist silver oxide.

When the reaction was carried out at  $0^\circ$ , a product was obtained (m. p.  $138$ – $140^\circ$ ) which, after crystallisation from alcohol (Found: Pt, 31.2. Calc. for  $C_8H_{20}I_2S_2Pt$ : Pt, 31.0%), gave a considerable proportion of  $\beta$ -base, together with diethyl sulphide, when treated with moist silver oxide (16 hours). The original material was therefore probably a mixture of the  $\alpha$ - and the  $\beta$ -di-iodide.

In another similar experiment, in which the  $\beta$ -base was treated below  $0^\circ$  with aqueous potassium iodide and then with a slight excess of dilute sulphuric acid, a brownish-yellow di-iodide, m. p.  $132$ – $135^\circ$ , was obtained. From methyl alcohol, it separated in minute yellowish-brown crystals, m. p.  $141$ – $143^\circ$ , which partly melted if plunged into a bath at  $125^\circ$ . With moist silver oxide, it gave a small proportion of  $\beta$ -base.

(4) When the  $\beta$ -dichloride was decomposed with aqueous silver sulphate, and to the filtered solution of the  $\beta$ -sulphate an excess of aqueous potassium iodide was added below  $0^\circ$ , a yellow di-iodide was precipitated. After extraction with benzene, however, the orange product was indistinguishable from the  $\alpha$ -di-iodide.

It must be concluded from these experiments that the  $\beta$ -di-iodide is easily transformed to the  $\alpha$ -isomeride.

*Tetrahalides.*—The  $\alpha$ -tetrachloride (XI) was prepared in quantitative yield by passing a slight excess of chlorine at  $0^\circ$  or at the ordinary temperature into a chloroform or benzene solution of the  $\alpha$ -dichloride. The crude product had m. p. ca.  $196^\circ$  (decomp.); it

separated from ethyl alcohol in lemon-yellow needles or in massive rectangular tablets belonging to the cubic system. The pure substance melts and decomposes at  $198^{\circ}$ , with sintering from  $188^{\circ}$ . It is readily soluble in benzene, from which it crystallises unchanged in cubic tablets (Found: C, 18.85; H, 4.25; Pt, 37.5.  $C_8H_{20}Cl_4S_2Pt$  requires C, 18.55; H, 3.9; Pt, 37.7%).

The  $\beta$ -tetrachloride (XII) was similarly obtained from the  $\beta$ -dichloride. The crude product melted between  $120^{\circ}$  and  $130^{\circ}$  but contained some  $\alpha$ -tetrachloride. Crystallised from benzene, in which it is much less soluble than the  $\alpha$ -isomeride, it separates in jagged, light-yellow prisms or (more slowly) in compact prisms capped by pyramids, the crystals being cubic (Found: C, 18.75; H, 4.2; Pt, 37.6, 37.9%). The powdered crystals melt completely when plunged into a bath at  $135^{\circ}$ ; the yellow melt then resolidifies, the solid melting again near  $195^{\circ}$ . When boiled with methyl or ethyl alcohol for a short time, it is changed to the  $\alpha$ -tetrachloride, which separates in the pure state; but it may be crystallised from ethyl alcohol by momentary heating and cooling, whereupon it separates in small, greenish-yellow, glistening platelets, melting first at  $133^{\circ}$  and then near  $198^{\circ}$ . The mixed m. p. of the two specimens of  $\alpha$ -tetrachloride, prepared (i) directly and (ii) through the  $\beta$ -tetrachloride, was the same as that of either.

The  $\alpha$ -tetrabromide,  $PtBr_4(SET_2)_2$ , obtained quantitatively by the action of bromine on a chloroform solution of the  $\alpha$ -dibromide, crystallises from ethyl alcohol in lustrous scarlet needles, sintering from  $192^{\circ}$  and melting at  $198^{\circ}$  (decomp.) (Found: C, 14.0; H, 2.95; Pt, 28.0.  $C_8H_{20}Br_4S_2Pt$  requires C, 13.8; H, 2.9; Pt, 28.1%); it is much more readily soluble in benzene than the  $\beta$ -form.

The  $\beta$ -tetrabromide,  $PtBr_2(SET_2Br)_2$ , was obtained by adding at  $0^{\circ}$  a slight excess of bromine in pure chloroform or, better, in benzene, to a solution of the  $\beta$ -dibromide in the same solvent. The crude product melted completely and resolidified in a few seconds if plunged into a bath at  $135^{\circ}$ , but if plunged at  $115^{\circ}$  and then heated it was changed without melting to the  $\alpha$ -isomeride. It separated from warm benzene in light red, flat, prismatic needles (Found: C, 13.6; H, 2.95; Pt, 27.8, 28.05%), which melted if plunged at  $125^{\circ}$  and then resolidified to the  $\alpha$ -compound, melting again at about  $195^{\circ}$ . When crystallised once from ethyl alcohol, it was changed to the  $\alpha$ -form, the m. p. and mixed m. p. with that substance being identical. This  $\beta$ -compound is more easily changed to the  $\alpha$ -form than is the  $\beta$ -tetrachloride. It should not be heated longer than a few seconds to effect solution even with benzene.

*Dichlorodibromides.*—In the following reactions addition of halogen to the dihalides was carried out in solution in alcohol-free



chloroform, in pure benzene, or in a mixture of chloroform and ligroin. Experiments indicated that benzene was the best solvent and that undue excess of halogen was to be avoided. In all cases the solvent was at once evaporated at the ordinary temperature, the product was quickly dried, and its m. p. observed. The whole product was then crystallised from pure benzene with momentary heating, and the crops were examined as to colour, crystalline form, and m. p. In all cases identities were checked by these means and by mixed m. p.'s and analyses.

(1) *Action of chlorine on the  $\alpha$ -dibromide.* The crude  $\alpha$ -dichlorodibromide (XX) separated as a mass of crystals, m. p. 190—193° (decomp.; after sintering). Crystallised from benzene, in which it was readily soluble, it separated in massive orange-red rhombs showing square and hexagonal faces. The powdered substance, which was strongly triboelectric, showed no signs of melting when plunged into a bath at 140°. It softened somewhat above 185° and melted at 190—193° (decomp.). It separated readily from ethyl alcohol in prismatic crystals, m. p. 192—193° (decomp.); but examination of the mother-liquors showed that the substance is partly reduced by alcohol, the use of which is therefore to be avoided in this connexion (Found: Pt, 31.8, 32.1, 32.3.  $C_8H_{20}Cl_2Br_2S_2Pt$  requires Pt, 32.2%). Even from benzene the substance should not be recrystallised more than once.

(2) *Action of bromine on the  $\alpha$ -dichloride.* The crude product consisted of crystals of the same  $\alpha$ -dichlorodibromide, m. p. 189—192° (decomp.) after sintering. The crystals from alcohol or from benzene were those of (XX). Analyses were carried out after one crystallisation from benzene (Found: C, 16.1; H, 3.65; Pt, 32.15, 32.1%) and then after a recrystallisation from the same solvent (Found: Pt, 31.8. Calc.: C, 15.8; H, 3.3; Pt, 32.2%).

(3) *Action of chlorine on the  $\beta$ -dibromide.* The crude orange-yellow crystalline product, which was thrown out of solution when chlorination was carried out at 0° in benzene, consisted of the  $\beta$ -dichlorodibromide (XIX), melting completely when plunged into a bath at 105° and then resolidifying and again melting near 188°. When crystallised from ethyl alcohol, it was completely changed to the  $\alpha$ -isomeride (XX); but it could be crystallised by momentary warming with benzene, from which it separated in small, dark yellow, complex prisms or in rhomboidal platelets melting if plunged at 110°, or near 120° (incompletely) if heated in the ordinary way (Found, in different preparations: C, 15.5; H, 3.4; Pt, 31.8, 32.1%). A mixture with the isomeric  $\beta$ -dichlorodibromide (XXI, below), m. p. 125°, melted completely if plunged into a bath at 115°, but if heated in the ordinary way melted only at 190—192°. This

dichlorodibromide was much less permanent than (XXI), changing, even on a few minutes' boiling with benzene, into the  $\alpha$ -isomeride, which was shown to be identical with (XX).

(4) *Action of bromine on the  $\beta$ -dichloride.* The crude product consisted of a mass of salmon-yellow prisms of the  $\beta$ -dichlorodibromide (XXI), completely melting when plunged at  $128^\circ$ , resolidifying, and again melting near  $188^\circ$ . Crystallised from benzene, in which it was much less soluble than the  $\alpha$ -isomeride, it separated in complex prisms, m. p.  $125^\circ$  (with resolidification), of salmon-yellow shade, showing rhomboidal faces (Found: C, 15.8; H, 3.35; Pt, 32.25%). One crystallisation from ethyl alcohol or 10 minutes' heating in solution in benzene changed it completely to the  $\alpha$ -form, which was again proved to be identical with (XX). This  $\beta$ -dichlorodibromide, which is of darker shade than (XIX), can be kept in the solid state for several days without suffering more than slight change to the  $\alpha$ -form.

All four of the  $\beta$ -tetrahalides prepared were easily wetted and decomposed by concentrated nitric acid, in marked contrast to the  $\alpha$ -tetrahalides, which were remarkably stable to the warm reagent.

In solution, the  $\alpha$ -tetrahalides are probably in equilibrium with small proportions of the partly ionised  $\beta$ -tetrahalides, for the  $\alpha$ -dichlorodibromide tends to pass after many crystallisations from benzene into an  $\alpha$ -chlorotribromide, large ruby-red prisms from benzene, m. p.  $196^\circ$  (decomp.) (Found: C, 15.05; H, 3.2; Pt, 30.0, 29.9.  $C_8H_{20}ClBr_3S_2Pt$  requires C, 14.75; H, 3.1; Pt, 30.0%).

*Equimolecular mixture of the  $\alpha$ -tetrachloride and  $\alpha$ -tetrabromide.* The mixed substances, intimately ground together, had the same m. p. as the  $\alpha$ -dichlorodibromide (XX), and it was practically unaltered when the latter was added to the mixture. Crystallisation from alcohol (Found: Pt, 31.7%) or benzene gave products very similar to those obtained by crystallising (XX) from the same solvent. It will be seen that the  $\alpha$ -tetrachloride does not depress to a normal extent the m. p. of the  $\alpha$ -tetrabromide, and this phenomenon is to be expected (compare J., 1928, 512). It is uncertain, therefore, whether an equimolecular mixture of these substances would depress to any noticeable extent the m. p. of a true  $\alpha$ -dichlorodibromide (XX). There remains the possibility that (XX) is produced when the mixture crystallises, or that mixed crystals of the two tetrahalides, indistinguishable from (XX) by the means employed, are formed. Again, it is possible that at temperatures near  $180^\circ$  the  $\alpha$ -dichlorodibromide (XX) becomes changed into an equimolecular mixture of the two simple  $\alpha$ -tetrahalides. The matter will be further examined.

*Physico-chemical Measurements.*

*Molecular Weights.*—These determinations were made to show that the isomerism of the  $\alpha$ - and  $\beta$ -salts could not be explained by supposing that one was a polymeride of the other, this view of the relationship of certain 4-co-ordinated platinum compounds being maintained by Reihlen and Nestle (*Z. anorg. Chem.*, 1927, **159**, 343; *Annalen*, 1926, **447**, 21, 312, 448).

The benzene used was supplied by the British Drug Houses, Ltd., especially for molecular-weight determinations. Traces of moisture were removed by distillation over phosphoric oxide (compare Sidgwick, J., 1920, **117**, 1340). A determination with naphthalene in this solvent gave  $M$ , 128.2. The  $\alpha$ - and  $\beta$ -salts were analytically pure and their m. p.'s were unchanged by successive recrystallisations from light petroleum (b. p. 40–60°) in the case of the  $\alpha$ -, and from hot benzene in the case of the  $\beta$ -form, benzene of crystallisation being afterwards removed [Found: for  $\alpha$ -salt,  $M$ , 434; for  $\beta$ -salt,  $M$ , 438.  $\text{PtCl}_2(\text{SEt}_2)_2$  requires  $M$ , 446.5].

*Conductivity Measurements.*—These determinations, which required special care on account of the small solubility of the substances in water, could not be accurately made by the use of a Kohlrausch slide wire. To overcome these and other disadvantages, a substitution bridge, constructed by Messrs. Tinsley and Son to the specifications of Mr. H. M. Spittle of this Department, was employed.

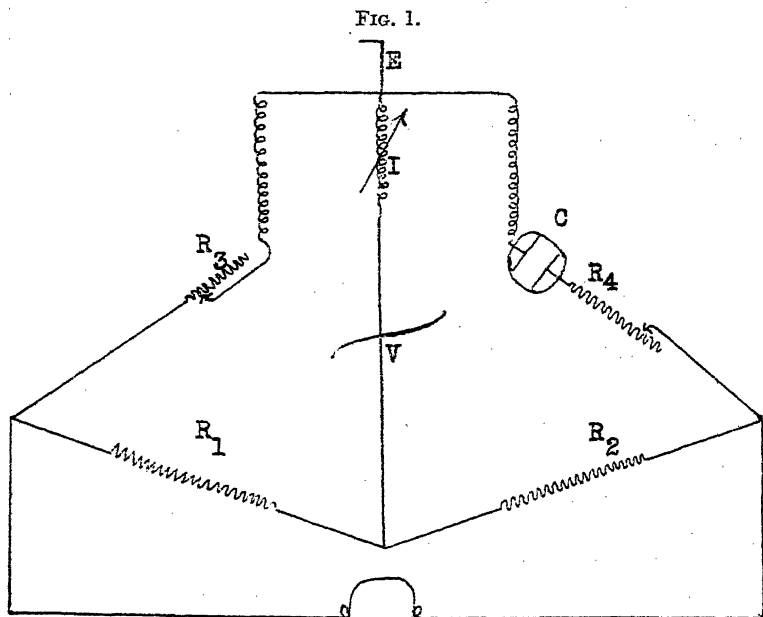
The arrangement of the apparatus is outlined in Fig. 1.

A valve oscillator, V, producing a pure sine wave of 1000 cycles, formed the source of alternating current, all capacity effects being eliminated by the use of two fixed inductances and one variable inductance, I, the effective inductance of which balanced the capacity of the liquid in the conductivity cell, C. Two 2000-ohm non-inductive resistances,  $R_1$  and  $R_2$ , formed two arms of the bridge, the third,  $R_3$ , consisting of a variable non-inductive resistance of 0–11,000 ohms. The fourth contained another variable non-inductive resistance of 0–10,000 ohms,  $R_4$ , which could be coupled with the cell, and, where necessary,  $R_3$  and  $R_4$  were increased by the introduction of additional, standardised non-inductive resistances. Readings were made by altering  $R_3$ , so that a balance was obtained with  $R_4$  about 50 ohms, when in series with the cell. By eliminating the cell, the true value of  $R_3$  was determined, the difference between the two readings giving the actual resistance of the cell, although the total resistance of the bridge remained unaltered. In this way successive readings of a resistance of any magnitude never fluctuated by more than 0.1%.

*Conductivity water.* The water used possessed a conductivity of

$3.1 \times 10^{-6}$  mho at  $18^\circ$ , and this did not materially increase during the course of several weeks.

*Conductivity vessel.* The conductivity vessel was constructed to hold 5 c.c. of liquid and fitted with a ground-glass stopper. After being washed with conductivity water, the vessel was dried in a vacuum desiccator, which was then opened in a slow stream of carbon dioxide-free air. Dilutions ( $v$ ) are given in litres per g.-mol., and the temperature was  $18^\circ$  in each case.



*Results.* Solutions of the  $\beta$ -dichloride were prepared in two ways: (a) by warming to  $30^\circ$ , followed by cooling to  $18^\circ$  (the solution was not acid to litmus or Congo-red paper), and (b) by shaking the salt (2 mg.) with water (5 c.c.) in the cell over-night.

	$v$ .	$\mu$ .		$v$ .	$\mu$ .
$\beta$ -Dichloride (solution a)	658.2	43.4	$\beta$ -Oxalate	355.3	18.6
" ( " b)	1037	50.9	$\beta$ -Base	276.4	11.4
" ( " b)	1178	50.4		115.0	7.2

Werner and Herty's conductivity data (*Z. physikal. Chem.*, 1901, 38, 347) for the diammines of platinous chloride are of interest in connexion with our results for the dichloride. Their initial values for  $\mu$  for the *cis*-form were low ( $\mu$  2–4) provided that the solution was prepared at  $25^\circ$ , but if it was first heated to  $50^\circ$  and then cooled to  $25^\circ$  a value of *ca.* 40 was recorded. Owing to the minute solu-

bility of the *trans*-form in water at 25°, they could not obtain suitable solutions for conductivity measurements by operating at this temperature, but they found that if the salt was dissolved in water at 50° and the solution then cooled to 25°, a conductivity of about 40 was registered. Hence they inferred by analogy with the behaviour of the *cis*-form that, if direct solution could have been effected at 25°, the *trans*-form would have been a non-electrolyte. Their statement that the *cis*- and *trans*-diammines are non-electrolytes is based, therefore, on analogy rather than on direct experimental evidence.

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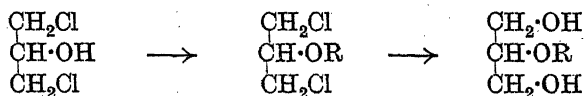
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EDGECASTON.

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LI.—*The Partial Esterification of Polyhydric Alcohols.*  
*Part X. The Discovery of the First True  $\beta$ -Glyceride,*  
*and the Untrustworthiness of the Supposed Structures*  
*of Certain Diglycerides.*

By ARTHUR FAIRBOURNE.

THE following method of synthesising  $\beta$ -derivatives of glycerol has formerly been regarded as trustworthy for  $\beta$ -esters (Grün, *Ber.*, 1910, 43, 1288), although untrustworthy for  $\beta$ -ethers (Gilchrist and Purves, *J.*, 1925, 127, 2735):



In Part V (*J.*, 1926, 3148), however, it was shown to produce  $\alpha$ - instead of  $\beta$ -esters, and the publication of this result was followed by claims of the discoveries of the first true  $\beta$ -ester of glycerol (Helferich and Sieber, *Z. physiol. Chem.*, 1927, 170, 31; 1928, 175, 311) and also of the first true  $\beta$ -ether (Hill, Whelen, and Hibbert, *J. Amer. Chem. Soc.*, 1928, 50, 2235; Hibbert, Whelen, and Carter, *ibid.*, 1929, 51, 302).

In Part IX (*J.*, 1929, 2232) it was shown, on the other hand, that the method was trustworthy for the preparation of the  $\beta$ -ethers, thus precisely reversing the relative values assigned to the reaction in

the literature; and it was incidentally realised that the credit of synthesising the first true  $\beta$ -ether of glycerol is apparently due to Gilchrist and Purves (*loc. cit.*), who, however, mistakenly recorded their experiment as a failure instead of as a success.

An almost parallel re-investigation of this synthesis has now been independently carried out by Hibbert and Whelen (*J. Amer. Chem. Soc.*, 1929, **51**, 1943), who, reasoning from the evidence considered in Part VII of this series, studied the same reactions and reached identical conclusions. These authors, however, effected their final hydrolysis by a modified process which involved a treatment with acid. Since alkaline conditions frequently favour migratory changes, it is very doubtful whether acidic conditions ought thus to be substituted for them, in seeking to prove that migrations could not have occurred in Gilchrist and Purves's work. On the other hand, the introduction of acid has greatly improved the yield obtainable from these reactions, which therefore now constitute a trustworthy process for preparing true  $\beta$ -ethers of glycerol without the formation of their  $\alpha$ -isomerides.

If the conclusion reached in Part V (*loc. cit.*) is correct, that all the preparations of supposed " $\beta$ "-monoglycerides known in 1926 were illusory, Helferich and Sieber would appear to be justified (*loc. cit.*) in claiming that they have now isolated the first true  $\beta$ -glyceride ever obtained.

It is clearly desirable, for this and other reasons, that all supposed esterifications in the  $\beta$ -position of glycerol should be subjected to careful scrutiny, and the present paper consists of an inquiry into some of these cases.

Esters of inorganic acids, such as the nitrates and phosphates, have not normally been contemplated in connexion with the general statements referring to " $\beta$ "-monoglycerides and " $\beta$ "-mono-esters made in this series of papers, but " $\beta$ "-monochlorohydrin has necessarily been taken into consideration, to some extent, as an intermediate product in one of the suggested syntheses investigated in Part V (*loc. cit.*). Prepared by the method of Hanriot (*Ann. Chim.*, 1879, **17**, 76), the particular specimen employed in that investigation was proved by its *p*-nitrobenzoate to consist almost entirely of the unwanted  $\alpha$ -isomeride. Henry (*Bull. Acad. roy. Belg.*, 1897, **33**, 110), however, apparently succeeded in differentiating between samples of these isomerides by reducing them to propylene glycol and trimethylene glycol, respectively. Read and Hurst (*J.*, 1922, **121**, 989) also describe a preparation of the " $\beta$ "-monochlorohydrin, but give no satisfactory proof of the structure of their product. Smith and Samuelsson (*Z. physikal. Chem.*, 1918, **92**, 717; 1920, **94**, 691, 723) have shown that the proportion of the

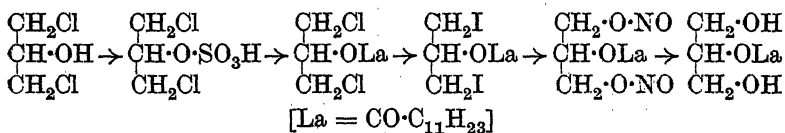
isomerides which are produced when glycerol and hydrogen chloride react upon one another varies with the conditions adopted.

No record has been found of any attempt to prepare a  $\beta$ -monoglyceride from a veritable specimen of  $\beta$ -monochlorohydrin by the method Grün suggested (*loc. cit.*), although Delaby and Dubois recently contemplated this synthesis (*Compt. rend.*, 1928, **187**, 949) in connexion with their belief that the  $\beta$ -mono-ester predominates when glycerol and formic acid react; nor is it thought likely that such an attempt will succeed, since a preferential production of  $\alpha$ -mono-esters is usual whenever intermediate  $\alpha\beta$ -rings can occur (compare Part V, *loc. cit.*; Part VII, J., 1929, 129; Part IX, *loc. cit.*).

Grün considered, however, that the trustworthiness of his alternative process for preparing  $\beta$ -monoglycerides, based on the reactions discussed at the beginning of this paper, had been experimentally confirmed (*loc. cit.*) by his resulting " $\beta$ "-monolaurin reacting with phenylcarbimide, and by his " $\alpha$ "-monolaurin not doing so.

This reaction has therefore been re-investigated: it is found that both the  $\alpha$ - and the " $\beta$ "-monolaurin prepared by his method can yield diphenylurethanes, which are identical, since no depression of melting point is caused when they are mixed.

Thieme also synthesised a " $\beta$ "-monolaurin by a modification of Grün's process (*J. pr. Chem.*, 1912, **85**, 284):



Comparison of his product with an authentic specimen of  $\alpha$ -monolaurin led him to believe that they were different substances; he consequently extended his researches to include the corresponding " $\alpha\beta$ "- and " $\alpha\gamma$ "-dilaurins, which, again, he found to be different from each other. Finally (*loc. cit.*) he investigated the disintegration of trilaurin by sulphuric acid, and estimated the proportions of the various partly esterified laurins produced in that reaction.

The whole of this work is shown in the following experimental portion to rest on a double fallacy, since the " $\beta$ "-monolaurin obtainable by his method is undoubtedly identical with  $\alpha$ -monolaurin, when pure, and the supposedly isomeric " $\alpha\beta$ "- and " $\alpha\gamma$ "-dilaurins are identical with each other also.

The controversy which arose between Grün and Thieme (*Ber.*, 1912, **45**, 3691; 1913, **46**, 1653, 2198) is thus largely explained: both authors correctly recognised the same material as the one

they had synthesised, and each insisted on the structure which his own preparation appeared to support.

To make the evidence of identity more definite, Thieme's intermediate  $\alpha\gamma$ -di-iodohydrin  $\beta$ -monolaurate has now been synthesised in another way, and obtained for the first time as a solid. This was hydrolysed, like the crude material, to  $\alpha$ -monolaurin, which was again identified by a mixed melting point.

Another supposed  $\beta$ -monoglyceride is " $\beta$ "-monomyristin, isolated by Grün, Schreyer, and Weyrauch (*Ber.*, 1912, 45, 3420). Their preparation has therefore been repeated, and the product compared with an authentic specimen of  $\alpha$ -monomyristin obtained by the method of Fischer, Bergmann, Bärwind, and Pfähler (*Ber.*, 1920, 53, 1589, 1606, 1621). Both are identical.

Further, the corresponding " $\alpha\beta$ "- and " $\alpha\gamma$ "-dimyristins described by Grün and Theimer (*Ber.*, 1907, 40, 1792) have now been prepared by the recommended processes, and the samples obtained are again identical with each other.

A precisely similar case to the laurins and the myristins is that of the margarins, all five of which have recently been described by Thomson (*Trans. Roy. Soc. Canada*, 1926, 20, III, 445):

- |      |                                   |                                   |
|------|-----------------------------------|-----------------------------------|
| I.   | $\alpha$ -Monomargarin            | } m. p. 76°, $n_D^{20}$ 1.441.    |
| II.  | " $\beta$ "-Monomargarin          |                                   |
| III. | " $\alpha\beta$ "-Dimargarin      | } m. p. 70—72°, $n_D^{20}$ 1.439. |
| IV.  | $\alpha\gamma$ -Dimargarin        |                                   |
| V.   | $\alpha\beta\gamma$ -Trimargarin. |                                   |

By analogy with the cases just cited, and also from a consideration of the methods of preparation adopted for these glycerides, it is very probable (see Part V) that (I) and (II) should be identical, and (see Parts VII and VIII) that (III) and (IV) should be identical with each other also.

The eight recorded determinations of physical constants summarised in the above table appear to establish these identities, and make it clear that only two out of the four possible partly esterified margarins have really been isolated. (Mixed melting points would, however, still be desirable in confirmation of these identities.)

Among other similar cases of supposed isomerism, believed to be due to esterification in the  $\beta$ -position, may be mentioned the " $\alpha\beta$ "- and " $\alpha\gamma$ "-dipalmitins and the " $\alpha\beta$ "- and " $\alpha\gamma$ "-distearins.

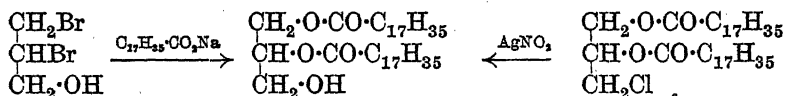
The " $\alpha\beta$ "- and " $\alpha\gamma$ "-structures are still separately assigned to these diglycerides in authoritative modern works of reference (*e.g.*, Ubbelohde's "*Handbuch der Öle und Fette*," 1929, vol. I, pp. 174—176), and the reactions concerned in their preparations are still often relied upon as satisfactory evidence of constitution (see



Thomson, 1928, *loc. cit.*; Delaby and Dubois, *Compt. rend.*, 1928, **187**, 767, who now record the syntheses of " $\alpha\beta$ "- and " $\alpha\gamma$ "-diformates in these ways; also the work of Grün and Limpächer described below; and the applications of these reactions to the preparations of "symmetrical" and "unsymmetrical" mixed triglycerides by Whitby, J., 1926, 1458, by Humnicki and Lunkiewicz, *Bull. Soc. chim.*, 1929, **45**, 422, and by Weizmann and Haskelberg, *Compt. rend.*, 1929, **189**, 104).

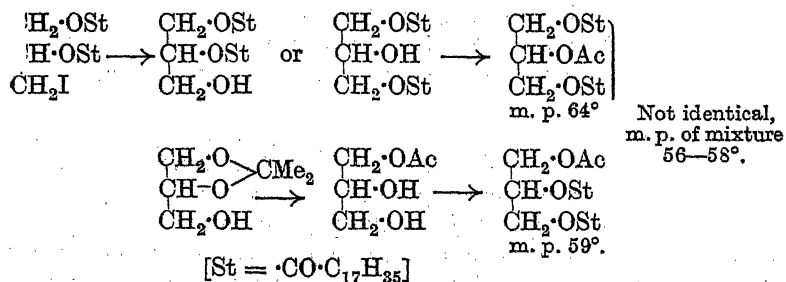
Their syntheses have therefore been re-investigated, and the expected identities experimentally proved.

Thus, in the typical case of the distearins, the " $\alpha\beta$ "-isomeride is described as having been synthesised both from  $\alpha\beta$ -dibromohydrin by Guth (*Z. Biol.*, 1903, **44**, 78) and by Renshaw (*J. Amer. Chem. Soc.*, 1914, **36**, 537), and also from the  $\alpha\beta$ -distearate of monochlorohydrin by Grün and Theimer (*Ber.*, 1907, **40**, 1792):



Repetition of these two processes has now produced specimens of the supposed " $\alpha\beta$ "-distearin, melting, alone or mixed, at 78—79°; but the  $\alpha\beta$ -structure cannot be regarded as confirmed by this agreement (compare Part VII), since the same distearin, again causing no change in mixed melting point, has also been obtained from  $\alpha\gamma$ -dichlorohydrin by a repetition of the synthesis of " $\alpha\gamma$ "-distearin described by Guth (*loc. cit.*).

Fischer (*Ber.*, 1920, **53**, 1621) employed the  $\alpha\beta$ -distearate of moniodohydrin, instead of that of monochlorohydrin, in a reaction which is very similar to one of the three just mentioned, but he diagnosed the unexpected " $\alpha\gamma$ "-structure of his product indirectly from the difference in physical properties of its acetate and of  $\alpha$ -acetoxy- $\beta\gamma$ -distearin synthesised in another way:

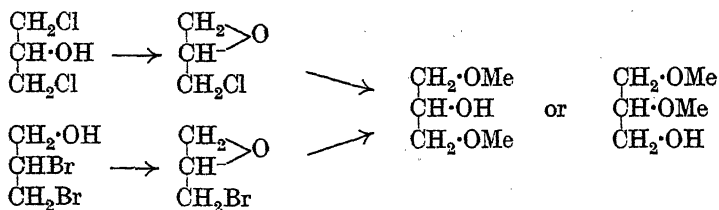


The identity of the samples of the " $\alpha\beta$ "- and " $\alpha\gamma$ "-distearins now obtained is thus fully in accord with Fischer's interpretation

of his experiment, and with his prophecy that the " $\alpha\beta$ " mixed diglycerides of Grün and Schreyer (*Ber.*, 1912, **45**, 3420) will probably be found to have the  $\alpha\gamma$ -structure; moreover, it explains Renshaw's confidence (*loc. cit.*) that Hundeshagen (*J. pr. Chem.*, 1883, **28**, 219) must have isolated at least a small quantity of the " $\alpha\beta$ "-isomeride from his direct esterification of glycerol with stearic acid; it explains the similar claim of Kreis and Hafner (*Ber.*, 1903, **36**, 1123); but it discredits, for example, the constitution of the glyceride phosphate recorded by Renshaw and Stephens (*J. Amer. Chem. Soc.*, 1914, **36**, 1770).

No suggestion is now made that both possible isomerides may not be present to some extent in the crude products obtained from any, or indeed from all, of these reactions; all that is claimed in this connexion is that various processes separately recommended for the preparations of the " $\alpha\beta$ "- and " $\alpha\gamma$ "-dilaureins, -dimyristsins, -dipalmitins, and -distearins have produced specimens which, when purified, are identical with their supposed isomerides in every case.

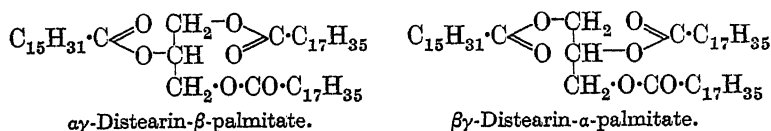
Two of the reactions now under consideration can also give rise to identical glycerol di-ethers (Part VIII, J., 1929, 1151; Gilchrist and Purves, J., 1925, **127**, 2735). Since, in this case, no subsequent wandering of acyl groups can occur, these identical products must result directly from the syntheses themselves, and the explanation would consequently seem limited to the assumption that an  $\alpha\beta$ -oxide is formed (Part IX, *loc. cit.*),



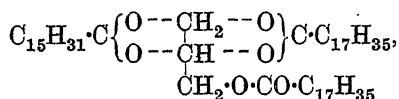
an assumption which is strengthened by the experimental proof that initial substitution of its  $\alpha\beta$ -oxide, epichlorohydrin, for the dichlorohydrin does not affect the identity of the product obtained (Part VIII).

The formation of these intermediate  $\alpha\beta$ -oxides can doubtless occur also during the similar preparations of the glycerol esters. In addition, however, interchanges of acid radicals, with one another and also with different radicals, take place so easily (see Part VII) that an explanation of these changes, not involving a large or difficult movement of heavy radicals such as the stearyl and palmityl groups, is much needed.

If the tendency towards the formation of ortho-esters is taken into consideration (see Parts VII and IX), these changes can readily be represented merely by a rearrangement of valencies in which little or no actual migration or relative movement of the atoms themselves has to be presumed.

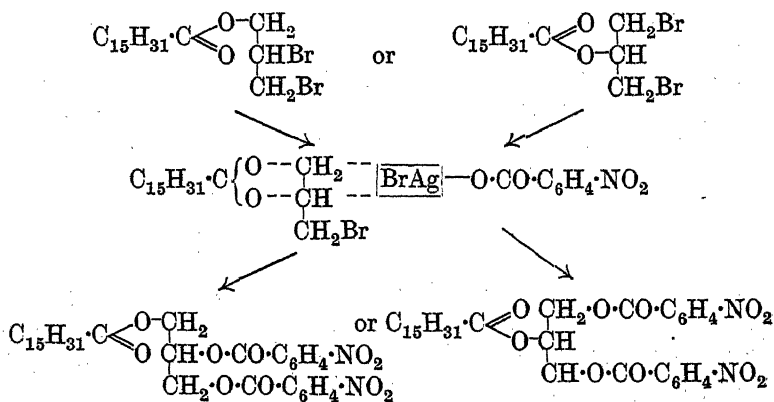


If conditions can exist in which the Hantzsch type of carboxyl group (*Ber.*, 1917, 50, 1422; Part VII, *loc. cit.*) actually occurs, the above two formulæ may even become identical,

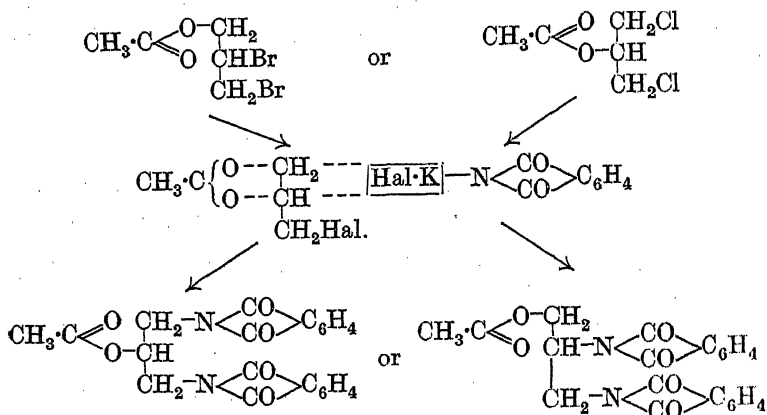


and, in any case, a tendency towards the transitory formation of such  $\alpha\beta$ -oxidic rings would seem very probable.

It is specially noteworthy, moreover, that these "migrations" appear to take place most readily *while other reactions are in progress*: the "migration" of an acyl radical occurring simultaneously with the elimination of a halogen atom from a glycerol molecule, even if the latter does not contain a hydroxyl group, is frequently experienced (Part VII), but could not previously be explained. Such reactions, however, for example, the formation of identical di-*p*-nitrobenzoates from  $\alpha\beta$ - and  $\alpha\gamma$ -dibromohydrin palmitates (Part VII),

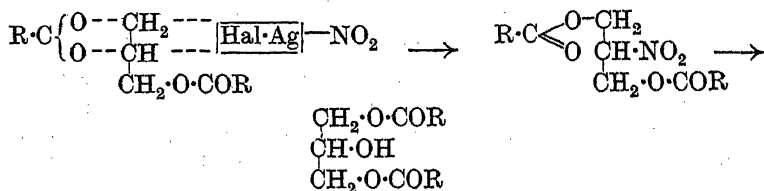


and of identical diphthalimido-compounds from the  $\alpha$ - and  $\beta$ -acetates of halogenohydrins (Part VII),

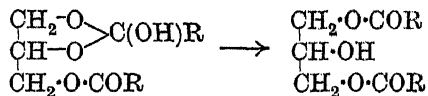


can easily be represented in this way.

The formation of  $\alpha$ -diglycerides, by the esterification and subsequent elimination of the halogen atoms of  $\alpha$ -monochlorohydrin and  $\alpha$ -monoiodohydrin, discussed earlier in this paper, can similarly be explained,



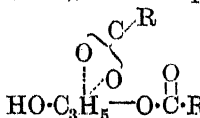
but in such cases, *where a free hydroxyl group is present or is produced*, a somewhat similar explanation has already been put forward tentatively by Fischer (*Ber.*, 1920, 53, 1621), the hydroxyl group being supposed by him to play an essential part in the mechanism of the change.



It is now clear, however, that these migrations occur whether a hydroxyl group is present or absent, and that a wider explanation is therefore required.

The only attempt to apply broadly the tendency towards the formation of ortho-esters to explain migratory changes in glycerides

appears to be that of Grün (*Ber.*, 1921, 54, 290), whose explanation,

however, involves the vague formula  for the

diglycerides themselves, instead of the simple mechanism now suggested.

In addition to complications arising (i) from the formation of intermediate glycidic rings, such as that in epichlorohydrin, mentioned earlier in this paper, and (ii) from the migratory effects just considered, there is also, in most syntheses, (iii) the possibility, due to the presence of metallic compounds, that hydrolyses and re-esterifications will take place rapidly (Fischer, Pfähler, and Brauns, *Ber.*, 1920, 53, 1634; Part III, J., 1925, 127, 2759). It is therefore thought that the  $\alpha\beta$ -formula should be accepted as representing the structure of any particular diglyceride only when optical rotation can be demonstrated, or when some other physical difference from the  $\alpha\gamma$ -isomeride, such as the depression of the latter's melting point, can be proved (compare Part VII).

Even in the event of an optical rotation being detected, caution should still be observed: Grün and Limpächer, for example (*Ber.*, 1926, 59, 1350), synthesised a lecithin from a supposed " $\alpha\beta$ "-distearin, m. p. 69°, the sulphuric ester of which had shown some evidence of containing an asymmetric material. The lecithin they obtained was afterwards found to be indistinguishable from that prepared from  $\alpha\gamma$ -distearin (*Ber.*, 1927, 60, 147). They further synthesised the corresponding kephalins (*ibid.*, p. 151), and were again unable to distinguish between their products.

A preparation of a sample of " $\alpha\beta$ "-distearin, with this melting point, and similarly made from its sulphuric ester, is described in detail by these authors in a later paper (*ibid.*, p. 264), but there is nothing in this description to prove that their product was a satisfactory specimen of the true  $\alpha\beta$ -isomeride as they supposed; it may have consisted, even substantially, of ordinary or  $\alpha\gamma$ -distearin, particularly as they mention that, during its final treatment, crystals were deposited which had the usual melting point of that compound.

The conclusions reached in Part V (*loc. cit.*), that every supposed isolation of a  $\beta$ -monoglyceride then recorded was probably illusory, and in Parts VII and IX (*loc. cit.*), that " $\alpha\beta$ - and  $\alpha\gamma$ -isomerism" in diglycerides is frequently accepted on insufficient evidence, are both thus fully confirmed, so far as the re-examination of " $\beta$ "-esters has yet been carried.

These conclusions, and the experimental evidence previously put

forward in their support, have recently been quoted in several connexions by Hibbert, Whelen, and Carter (*J. Amer. Chem. Soc.*, 1929, **51**, 304, 1602, 1606, 1944, 1945), who stress their importance in reaching an accurate view of the structures of glycerol compounds. It thus becomes increasingly clear that the relative values assigned to the various methods described in the literature for synthesising partly substituted glycerols require to be modified considerably, and a selection has consequently been made below, in accordance with the evidence obtained now and in the previous papers of this series, of what appear to be trustworthy processes for preparing  $\alpha$ -,  $\beta$ -,  $\alpha\beta$ -,  $\alpha\gamma$ -, and  $\alpha\beta\gamma$ -ethers and esters of definite structure:—

(i)  $\alpha$ -*Mono-ethers*, the structures of which were established by Irvine, Macdonald, and Soutar (*J.*, 1915, **107**, 337), are readily produced either by reacting upon monochlorohydrin with alkali and the requisite alcohol (Reboul, *Annalen Suppl.*, 1862, **1**, 238), or by the converse process (Parts I and III,\* *J.*, 1921, **119**, 1035; 1925, **127**, 2759; Cross and Jacobs, *J. Soc. Chem. Ind.*, 1926, **45**, 320r) of reacting upon sodium glyceroxide with the requisite halide.

The accidental production of higher ethers (Part III, *loc. cit.*) and of  $\beta$ -ethers (Part IX, *loc. cit.*) as by-products, however, is a complication arising from the use of sodium glyceroxide.

(ii)  $\beta$ -*Mono-ethers* may be prepared, as exemplified in the case of the  $\beta$ -methyl ether, by introducing an ethereal group either into  $\alpha\gamma$ -dichlorohydrin, or into certain other subsequently decomposable  $\alpha\gamma$ -compounds (Part IX, *loc. cit.*; Hibbert, Hill, Whelen, and Carter, *J. Amer. Chem. Soc.*, 1928, **50**, 2235; 1929, **51**, 302, 1943).

(iii)  $\alpha$ -*Monoglycerides* may conveniently be prepared from isopropylideneglycerol (Fischer, Bergmann, Bärwind, and Pfähler, *Ber.*, 1920, **53**, 1589, 1606, 1621), a synthesis which strongly indicates the  $\alpha$ -structure; confirmation being afforded by the rotatory evidence of Abderhalden and Eichwald (*Ber.*, 1915, **48**, 1847) and perhaps by the direct formation of these esters from allyl esters (Part IV, *J.*, 1926, 3146; Hibbert and Carter, *J. Amer. Chem. Soc.*, 1929, **51**, 1606).

They also result from the simple esterification of glycerol, or by the action of metallic salts on monochlorohydrin, but, in all such cases, are liable to be difficultly separable from higher glycerides occurring as by-products.

(iv)  $\beta$ -*Monoglycerides* were formerly believed to be obtainable by method (ii) above, but (see Part V, *loc. cit.*) the true  $\beta$ -isomerides have been produced by this method only when applied in a specially

\* These two papers, and also Parts II and VI (*J.*, 1921, **119**, 2076; 1926, 3240), were published under sectional titles only, and consequently were not numbered.

modified form, glycerol ditrityl ether being used as the initial  $\alpha\gamma$ -material (Helferich and Sieber, *loc. cit.*).

(v)  $\alpha\beta$ -*Diethers* of true structure have never been recorded (Part VIII, *loc. cit.*); successful methods for their preparation have been mentioned (Part IX, *loc. cit.*), and a further communication on this subject will be made later.

(vi)  $\alpha\gamma$ -*Diethers*. All syntheses yet recorded for glycerol diethers, whether " $\alpha\beta$ " or " $\alpha\gamma$ ," produce specimens which are identical after purification (Part VIII, *loc. cit.*) and can be proved to have the  $\alpha\gamma$ -structure by arguments not yet put forward.

(vii)  $\alpha\beta$ -*Diglycerides*. Of the various syntheses in the literature, only two would appear to be satisfactory: (a) indirect preparations from propylamines by Abderhalden and Eichwald and by Bergmann and co-workers (see Part VII, *loc. cit.*); (b) the method of Helferich and Sieber (*loc. cit.*) which employs glycerol  $\alpha$ -monotrityl ether.

(viii)  $\alpha\gamma$ -*Diglycerides*. With the exception of the methods of synthesis mentioned in (vii) above, all known preparations of diglycerides, whether by direct esterification or from chlorohydrins, etc., appear to produce the  $\alpha\gamma$ -isomerides preferentially, although many statements occur in the literature to the contrary. Probably a chemically pure  $\alpha\gamma$ -diglyceride is most conveniently prepared by Fischer's method (*Ber.*, 1920, **53**, 1621) from the  $\beta\gamma$ -di-ester of  $\alpha$ -iodohydrin.

(ix)  $\alpha\beta\gamma$ -*Tri-ethers and -esters*, containing different radicals, but of known constitution, are obtainable by mild methods (Fischer, *loc. cit.*) from the various types of partly substituted glycerols summarised above.

No investigation has yet been made to determine whether the alternative method of Whitby (*J.*, 1926, 1458) for synthesising "symmetrical" glycerides, also used by Thomson (*loc. cit.*), is affected by migratory changes such as have now been proved to occur in the very similar reactions considered in this paper and in Part VII (*loc. cit.*); for the same reasons the structures of the "symmetrical" and "unsymmetrical" triglycerides of Humnicki and Lunkiewicz (*Bull. Soc. chim.*, 1929, **45**, 422) and of Weizmann and Haskolberg (*Compt. rend.*, 1929, **189**, 104) must also be regarded as unproven.

#### EXPERIMENTAL.

$\alpha\gamma$ -*Di-iodohydrin  $\beta$ -Laurate*,  $C_{11}H_{23}\cdot CO\cdot O\cdot CH(CH_2I)_2$ .—(a) A crude material, believed to contain this substance, and obtained as an intermediate in the synthesis of " $\beta$ "-monolaurin, has been described by Thieme (*loc. cit.*); this complicated preparation has now been repeated, and the expected liquid obtained, but on hydrolysis, as stated below, it yielded  $\alpha$ -monolaurin instead of the  $\beta$ -isomeride.

(b) The pure *compound* has now been obtained as a colourless solid, m. p.  $34^{\circ}$  after recrystallisation from alcohol, by the direct esterification of  $\alpha\gamma$ -di-iodohydrin by the method described in Part V (*loc. cit.*) for the corresponding ester of  $\alpha\gamma$ -dichlorohydrin and for the *p*-nitrobenzoate of the latter (Found: C, 36.3; H, 5.6; I, 51.3.  $C_{15}H_{28}O_2I_2$  requires C, 36.4; H, 5.7; I, 51.4%).

$\alpha$ - and " $\beta$ "-*Monolaurin*,  $C_{11}H_{23}\cdot CO\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$ .—

(a) The supposed " $\beta$ "-monolaurin of Thieme was obtained from the crude  $\alpha\gamma$ -di-iodohydrin  $\beta$ -laurate as described by him. It unquestionably had the  $\alpha$ - and not the  $\beta$ -structure, however, since it melted at  $61$ – $62^{\circ}$ , alone or mixed with an authentic specimen of  $\alpha$ -monolaurin prepared by Fischer's method (*Ber.*, 1920, 53, 1600).

(b) The pure  $\alpha\gamma$ -di-iodohydrin  $\beta$ -laurate described above was also hydrolysed in an identical manner to  $\alpha$ -monolaurin, m. p., alone or mixed,  $61$ – $62^{\circ}$ .

$\alpha$ -*Monolaurin*  $\beta\gamma$ -*Diphenylurethane*,

$C_{11}H_{23}\cdot CO\cdot O\cdot CH_2\cdot CH(O\cdot CO\cdot NHPh)\cdot CH_2\cdot O\cdot CO\cdot NHPh$ .

—(a)  $\alpha$ -Monolaurin was warmed with excess of phenylcarbimide and kept for several days. The *diphenylurethane*, recrystallised from ligroin, melted at  $90^{\circ}$  (Found: C, 68.0; H, 7.9; N, 5.7.  $C_{29}H_{40}O_6N_2$  requires C, 67.9; H, 7.8; N, 5.5%).

(b) A sample prepared in an identical manner from the " $\beta$ "-monolaurin of Grün and Skopnik (*Ber.*, 1909, 42, 3750; see Part V, *loc. cit.*) melted, alone or mixed with (a), at  $90^{\circ}$ . The two samples therefore behave in the same way with phenylcarbimide, thus disposing of one of the arguments of Grün in support of the supposed " $\beta$ " structure of his preparation.

" $\alpha\beta$ "- and " $\alpha\gamma$ "-*Dilaurins*,  $(C_{11}H_{23}\cdot CO\cdot O)_2C_3H_5\cdot OH$ .—(a) A specimen of " $\alpha\beta$ "-dilaurin, prepared from  $\alpha$ -monochlorohydrin by Thieme's method (*loc. cit.*), melted at  $56^{\circ}$ .

(b) A specimen of " $\alpha\gamma$ "-dilaurin, prepared from  $\alpha\gamma$ -dichlorohydrin by Grün's method (*Ber.*, 1912, 45, 3691), melted, alone or mixed with (a), at  $56$ – $57^{\circ}$ , their identity thus being proved.

$\alpha$ - and " $\beta$ "-*Monomyristin*,  $C_{13}H_{27}\cdot CO\cdot O\cdot C_3H_5(OH)_2$ .—(a) The supposed " $\beta$ "-monomyristin of Grün, Schreyer, and Weyrauch (*Ber.*, 1912, 45, 3420) was prepared as described by them; it melted at  $68^{\circ}$ .

(b) An authentic specimen of  $\alpha$ -monomyristin was prepared from myristyl chloride and isopropylideneglycerol by means of the general method for preparing  $\alpha$ -mono-esters described by Fischer, Bergmann, Bärwind, and Pfähler (*Ber.*, 1920, 53, 1589, 1606, 1621). 10 G. of myristyl chloride were cautiously added with shaking to a mixture of 5.2 g. of isopropylideneglycerol and 5.8 g. of quinoline; after 2 days, the whole was treated with ether and the extract was



washed with *N*/2-sulphuric acid, potassium bicarbonate solution, then with water, and dried with anhydrous sodium sulphate. The product was shaken with hydrochloric acid (*d* 1.19); after crystallising several times from ether, it melted at 68°, alone or mixed with (a) (Found: C, 67.8; H, 11.1.  $C_{17}H_{34}O_4$  requires C, 67.6; H, 11.2%).

The supposed " $\beta$ "-monomyristin is therefore  $\alpha$ -monomyristin.

" $\alpha\beta$ "- and " $\alpha\gamma$ "-Dimyristin,  $(C_{13}H_{27}\cdot CO\cdot O)_2C_3H_5\cdot OH$ .—(a) The supposed " $\alpha\beta$ "-dimyristin prepared by the method of Grün and Theimer (*Ber.*, 1907, 40, 1792) melted at 64–65°.

(b) A specimen of " $\alpha\gamma$ "-dimyristin, prepared as described by the same authors (*loc. cit.*), also melted at 64–65°, alone or mixed with (a). Their two processes therefore gave rise to the same compound.

" $\alpha\beta$ "- and " $\alpha\gamma$ "-Dipalmitin,  $(C_{15}H_{31}\cdot CO\cdot O)_2C_3H_5\cdot OH$ .—(a) " $\alpha\beta$ "-Dipalmitin prepared from  $\alpha\beta$ -dibromohydrin by the method of Guth (*Z. Biol.*, 1903, 44, 78) melted at 69°.

(b) " $\alpha\gamma$ "-Dipalmitin prepared from  $\alpha\gamma$ -dichlorohydrin by a method also recommended by him (*loc. cit.*) melted at 69°, alone or mixed with (a). When pure, therefore, these specimens of Guth's " $\alpha\beta$ "- and " $\alpha\gamma$ "-dipalmitins are identical.

$\alpha\gamma$ -Dichlorohydrin  $\beta$ -Stearate,  $C_{17}H_{35}\cdot CO\cdot O\cdot CH(CH_2Cl)_2$ .—In an attempt to apply Grün's method for the synthesis of " $\beta$ "-mono-glycerides to the preparation of " $\beta$ "-monostearin, in a similar manner to that used in the previous investigations of the supposed " $\beta$ "-monolaurin, " $\beta$ "-monomyristin, and " $\beta$ "-monopalmitin,  $\alpha\gamma$ -dichlorohydrin was esterified by stearyl chloride in quinoline; the resulting  $\alpha\gamma$ -dichlorohydrin  $\beta$ -stearate, after crystallising from alcohol, melted at 39° (Found: C, 63.6; H, 10.0; Cl, 17.8. Calc. for  $C_{21}H_{40}O_2Cl_2$ : C, 63.8; H, 10.1; Cl, 18.0%).

Whitby (*J.*, 1926, 1458) obtained a compound of this melting point by treating epichlorohydrin with stearyl chloride, a result that must be regarded as an example of an acyl group spontaneously entering the  $\beta$ -position in the glycerol molecule. Humnicki also (*Bull. Soc. chim.*, 1929, 45, 279) prepared probably the same compound by direct esterification of dichlorohydrin with free stearic acid.

Attempts to hydrolyse this product to the  $\alpha$ - or " $\beta$ "-mono-glyceride, either by the method described in Part V (*loc. cit.*), or after preliminary treatment with potassium iodide such as was used in Thieme's process mentioned above, have been unsuccessful. It was recorded in Part V that, although the corresponding laurate and palmitate of  $\alpha\gamma$ -dichlorohydrin were successfully hydrolysed, the *p*-nitrobenzoate, the 3:5-dinitrobenzoate, and also the corresponding *p*-nitrobenzoate of  $\alpha\gamma$ -dibromohydrin could not be hydrolysed in that way. Grün was of opinion (*Ber.*, 1910, 43, 1288) that it is the esters of simple acids, such as acetic and benzoic

acids, which give only poor yields but it would appear that other radicals can produce the same effect. The stability of the halogen atoms is perhaps significant in connexion with the formation of  $\alpha\beta$ -oxidic rings (Part VII, *loc. cit.*) which account for some of the migratory changes that frequently occur. In this connexion there may also be mentioned the very stable  $\beta$ -methyl and  $\beta$ -trityl ethers of dichlorohydrin (Parts IX and VII), the distearate of monochlorohydrin (Grün and Theimer, *Ber.*, 1907, **40**, 1792), and the chloride of isopropylideneglycerol (Fischer and Pfähler, *Ber.*, 1920, **53**, 1606).

This ester also resisted an attempt to displace its chlorine atoms by means of potassium phthalimide in the manner described in Part VII.

" $\alpha\beta$ -" and " $\alpha\gamma$ "-Distearins,  $(C_{17}H_{35}\cdot CO\cdot O)_2C_3H_5\cdot OH$ .—(a) " $\alpha\beta$ "-Distearin has been prepared from  $\alpha\beta$ -dibromohydrin by the method of Guth (*loc. cit.*) and Renshaw (*J. Amer. Chem. Soc.*, 1914, **36**, 537), and obtained with the m. p. 78—79°.

(b) Another specimen of " $\alpha\beta$ "-distearin has been prepared from  $\alpha$ -chlorohydrin  $\beta\gamma$ -distearate by repeating the synthesis of Grün and Theimer (*loc. cit.*); it melted at 78—79°, alone or mixed with (a).

(c) " $\alpha\gamma$ "-Distearin was prepared from  $\alpha\gamma$ -dichlorohydrin by the method of Guth (*loc. cit.*; compare Bömer and Limpricht, *Z. Unters. Nahr. Genussmittel*, 1913, **25**, 354). This again melted at 78—79°, alone or mixed with either (a) or (b).

Throughout the work described in this paper, many recrystallisations from alternating solvents were frequently necessary in preparing specimens of supposed isomerides for mixed melting point determinations.

The author desires to express his indebtedness to the Chemical Society for a grant which has partly met the expenses incurred in this work.

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[Received, November 1st, 1929.]

### LII.—*Strychnine and Brucine. Part IX. Preparation of Some Isomerides of Dinitrostrychol and Trinitrostrychol.*

By JULIUS NICHOLSON ASHLEY, (the late) WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

IN 1898, Tafel (*Annalen*, **301**, 336) showed that, when strychnine was heated first with dilute and then with concentrated nitric acid, the base was nitrated and subsequently degraded, with the formation

of oxalic and picric acids, together with a compound,  $C_{10}H_5O_8N_3$ , considered to be  $C_9NH_2(OH)_2(NO_2)_2 \cdot CO_2H$  and termed dinitrostrycholcarboxylic acid.

The carboxyl group could be eliminated, or displaced by nitroxyl, dinitrostrychol,  $C_9NH_3(OH)_2(NO_2)_2$ , and trinitrostrychol,  $C_9NH_2(OH)_2(NO_2)_3$ , respectively being produced.

From the properties of these substances and of dinitrostrychol monomethyl ether, Tafel concluded that the hypothetical strychol is either a dihydroxyquinoline or a dihydroxyisoquinoline; he further considered that one of the hydroxyl groups is in proximity to a nitro-group and is responsible for the formation of the yellow neutral alkali-metal salts of dinitrostrychol and that the other hydroxyl exhibits a carbostyryl-like character and functions in the formation of the red alkaline-reacting salts. Finally, Tafel stated (*loc. cit.*, p. 300) that attempts to transform dinitrostrychol derivatives to known substances had been unsuccessful, and that synthetic experiments also had been fruitless; the details of the latter have not been published.

The work recorded in the present communication was completed in 1926, before there was any suggestion (Fawcett, Perkin, and Robinson, Part VII, J., 1928, 3082) that dinitrostrychol might be an isoquinoline derivative,\* and, at that time, we followed Tafel in regarding strychnine as a derivative of quinoline. It appeared highly improbable that the benzene ring of dinitrostrycholcarboxylic acid is not the original benzene ring of strychnine; brucine gives quite different products and nitric acid would not be expected to dehydrogenate the reduced rings of the alkaloid. The same argument applies to the picric acid which is formed alongside the dinitrostrycholcarboxylic acid. But the first action of nitric acid on strychnine is to nitrate it to dinitrostrychnine hydrate, which must then break down into picric acid and the strychol derivative. It follows from these considerations that the nitro-groups in dinitrostrychnine hydrate and dinitrostrycholcarboxylic acid are in the *m*-relation to each other.

On the assumption that dinitrostrychol is a dinitrodihydroxyquinoline, we can proceed a step further and restrict attention to the 6 : 8-dinitrodihydroxyquinolines, since the quinoline nitrogen atom would certainly be replaced by hydroxyl in the course of the reactions leading to the formation of picric acid from dinitrostrychnine hydrate. The same orientation follows from a consideration of analogies in connexion with the original nitration of strychnine; the

\* We have now a definite proof that the substance is a quinoline derivative. A communication on this subject will shortly be submitted to the Society.—R. R.

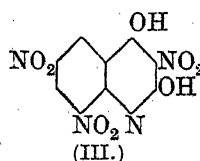
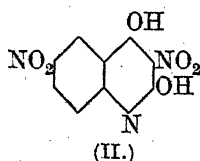
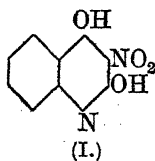
nitro-groups would, doubtless, enter the *op*-positions with respect to the nitrogen atom attached to the nucleus.

The positions 6 and 8 are therefore not possible situations for the hydroxyl groups of dinitrostrychol, and strychol might be 2:3-, 2:4-, 2:5-, 2:7-, 3:4-, 3:5-, 3:7-, 4:5-, 4:7-, or 5:7-dihydroxyquinoline.

Very little was known of the nitro-derivatives of such dihydroxyquinolines, and in order to study their properties we have synthesised some typical members of this group, selecting those representatives which had the best claim to be considered in connexion with the strychol problem.

The outcome has been to exclude the 2:4-, 2:5-, and 2:7-formulæ with certainty, and the 4:7-formula on somewhat less definite grounds. Of the remaining possibilities, all but the 2:3-, 3:4-, and 4:5-formulæ are highly improbable.

The first stage in the nitration of 2:4-dihydroxyquinoline was studied by Gabriel (*Ber.*, 1918, 51, 1500), who obtained 3-nitro-2:4-dihydroxyquinoline (I), and this substance has been found to yield 3:6(or 8)-dinitro-2:4-dihydroxyquinoline (II, 3:6) on further nitration in sulphuric acid solution. The introduction of a third nitro-group presented great difficulties, which were only surmounted after many unsuccessful experiments. The acetyl derivative of (II) was treated under special conditions with a mixture of 10% oleum and potassium nitrate, and the product was 3:6:8-trinitro-2:4-dihydroxyquinoline (III), an isomeride of trinitrostrychol.

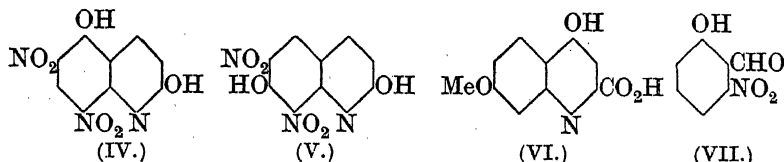


The constitution of the substance is proved by its conversion into picric acid by means of boiling nitric acid, and this reaction constitutes one of the distinctions from trinitrostrychol, which cannot be similarly degraded. Attempts to effect the ring closure of *ethyl* 3:5-dinitro-2-acetamidobenzoate, which would have afforded 6:8-dinitro-2:4-dihydroxyquinoline, were not successful.

6:8-Dinitro-2:5-dihydroxyquinoline (IV) and 6:8-dinitro-2:7-dihydroxyquinoline (V) were obtained from the corresponding amino-carbostyrls by diazotisation, decomposition, and nitration without isolation of intermediate stages.

Neither of these substances was identical with dinitrostrychol; they did not yield trinitro-compounds but suffered degradation on boiling with nitric acid and gave rise to styronic acid.

Compound (IV) was much more stable than (V), and the yield of the trinitroresorcinol was poor; the reaction is of interest in that it confirms the view that the quinoline nitrogen atom is replaced by hydroxyl in all such nitration-oxidation processes.



A synthesis of 4-hydroxy-7-methoxyquinoline-2-carboxylic acid (VI) has been effected, and the results obtained on nitrating this substance were not in agreement with the view that strychnol is 4:7-dihydroxyquinoline.

Further, in some preliminary experiments on the synthesis of 4:5-dihydroxyquinoline derivatives, the Tiemann-Reimer reaction was applied to *m*-nitrophenol, and 6-nitrosalicylaldehyde (VII) obtained in 3% yield. The orientation of this substance follows from the facts that it is not a *p*-hydroxybenzaldehyde, being volatile in steam, and that its methyl ether yields an indigotin derivative on treatment with acetone and sodium hydroxide.

#### EXPERIMENTAL.

*Dinitrostrycholcarboxylic Acid and Dinitrostrychol*.—The method of Tafel (*loc. cit.*) was modified in that the mixture of strychnine and 20% nitric acid was heated on the steam-bath for 120 hours; losses by evaporation were compensated by the addition of 20% nitric acid. Strychnine nitrate (115 g.), nitric acid (900 g., *d* 1.42), and water (3600 c.c.) gave ultimately 10.3 g. of pure dinitrostrycholcarboxylic acid.

A large number of analyses of dinitrostrycholcarboxylic acid, of dinitrostrychol and its methyl ether have been carried out, and Tafel's view of the composition of these substances is unquestionably correct.

Dinitrostrychol crystallises best from acetic acid, in very pale yellow needles, *m. p.* 282° (Tafel, *loc. cit.*, crystallised the substance from alcohol or nitric acid, and gives the *m. p.* 284°).

When dinitrostrychol is reduced in alcoholic solution with zinc dust and hydrochloric acid, the resulting colourless solution exhibits a strong bluish-violet fluorescence; it becomes discoloured rapidly, and, on dilution with water and the addition of ferric chloride, develops a deep red coloration, changing to reddish-brown.

Attempts to reduce only one nitro-group of dinitrostrychol were unsuccessful.

Complete degradation, without formation of picric or styphnic acid, resulted when dinitrostrychol (0.5 g.) was heated in a sealed tube at 200° with nitric acid (4 c.c., *d* 1.5) for 4½ hours. With the same quantities, heated at 120–125° for 2 hours, the product was pure trinitrostrychol.

Dinitrostrychol monomethyl ether (Tafel, *loc. cit.*, p. 345) was obtained by heating the dry monopotassium salt of dinitrostrychol (2 g.) with methyl iodide (5 c.c.) in a sealed tube at 155° for 2½ hours, or by refluxing a mixture of the monopotassium salt (4 g.), purified methyl sulphate (5 c.c.), and xylene (150 c.c.) for 1½ hours (yield, 70–75%; m. p. 194–195°).

The conditions for the hydrolysis of the methyl ether by aqueous sodium hydroxide have been studied, and the following experiments are typical. (1) The finely powdered methyl ether (0.2 g.) was triturated with cold aqueous sodium hydroxide (10 c.c. of 1%); very little material passed into solution. On heating at 40° for 2 minutes, an orange-red solution was obtained, and this was filtered and acidified, yielding dinitrostrychol free from its methyl ether. (2) The finely powdered methyl ether (0.2 g.), when triturated with cold aqueous sodium hydroxide (10 c.c. of 8%), was converted into a deep red, insoluble sodium salt. This was collected and treated with dilute sulphuric acid, yielding the original methyl ether, m. p. 192°. It is evident that the monomethyl ether possesses very weak acidic character, and is hydrolysed by aqueous alkalis with special facility.

Tafel (*loc. cit.*) made the very interesting observation that dinitrostrychol behaves as a dibasic acid towards baryta, since, although the potassium salt, stable in the presence of water, has the composition  $C_9H_4O_6N_2K$ , the barium salt under similar conditions appears to be  $C_9H_3O_6N_2Ba$ . This suggested to us that the hydroxyl groups are probably in the ortho- or peri-positions with respect to each other, and we attempted to confirm this view by the preparation of an ethylene ether or an oxalyl derivative of dinitrostrychol. The disodium salt (5 g.) was refluxed for 50 hours with ethylene dibromide (4 c.c.) and absolute alcohol (100 c.c.). Apart from unchanged dinitrostrychol, a relatively very small amount of a sparingly soluble substance, crystallising from alcohol in pale brown needles, m. p. 186–187° (Found: N, 15.0, 14.8%), was isolated. This substance exhibited the behaviour of dinitrostrychol monomethyl ether towards 1% sodium hydroxide solution and was probably the corresponding monoethyl ether (N, 15.1%).

The dipotassium salt of dinitrostrychol (2.9 g.) was mixed with oxalyl chloride (2 c.c.) (Staudinger, *Ber.*, 1908, 41, 3563) and pure toluene (10 c.c.); the initial reaction was controlled by cooling in

water and, after 12 hours, the mixture was heated on the steam-bath for 2 hours. The filtered liquid was evaporated under diminished pressure; the pale yellow residue, after being lixiviated with water, crystallised from toluene in very pale yellow, irregular prisms, m. p. 161° (Found: N, 19.5, 19.5%). Unfortunately, the yield was poor, so that a full examination was not possible, but it is clear that the action of the oxalyl chloride must have removed either carbon or oxygen or both from the dinitrostrychol molecule (dinitrostrychol,  $C_9H_5O_6N_3$ , requires N, 16.8%).

The substance was insoluble in cold aqueous sodium carbonate, but, on boiling, it dissolved to an orange solution; it was immediately soluble in cold dilute aqueous sodium hydroxide to an orange-red solution. On boiling with nitric acid ( $d$  1.42, boiled), oxidation occurred and the evaporated liquid gave, with a little water, long, pale yellow rods, m. p. 278–279° (decomp.) (Found: N, 15.3%, a provisional figure in the absence of a duplicate). This substance was readily soluble in cold dilute sodium carbonate to a deep orange solution.

It is very difficult to explain these remarkable results, and the subject merits further investigation.

Trinitrostrychol was found to be more readily obtainable by the nitration of dinitrostrychol than from dinitrostrycholcarboxylic acid (Tafel). It sufficed to heat a mixture of dinitrostrychol (0.5 g.) and nitric acid (5 c.c.,  $d$  1.5) on the steam-bath for 1 hour. On the addition of water (15 c.c.), the trinitrostrychol separated in pale yellow, microscopic needles, m. p. 218°. No trace of picric or styphnic acid was produced. The pale yellow solution in dilute aqueous sodium hydroxide rapidly darkened on heating and became deep brown. This characteristic behaviour is exhibited by traces of trinitrostrychol, and advantage has been taken of this fact in showing that certain synthetic products do not contain the substance.

*2:4-Dihydroxyquinoline and Derivatives.*—According to Camps (*Arch. Pharm.*, 1899, 237, 688), the action of sodium on methyl acetylanthranilate (Mehner, *J. pr. Chem.*, 1901, 64, 83) gives a 60% yield of crude 2:4-dihydroxyquinoline, but we find that the yield of pure substance barely exceeds 40%. Other methods, however, including those of Erdmann (*Ber.*, 1899, 32, 3570) and of D.R.-P. 11767, were still less satisfactory. Camps's method was slightly modified. Dry powdered methyl acetylanthranilate (50 g.) was added to granulated sodium (6 g.) suspended in toluene (200 c.c.). Reaction occurred and the yellow liquid boiled spontaneously. The mixture was finally refluxed (oil-bath) until it became viscous. After cooling, the solid was collected, freed as far as possible from toluene, and dissolved in water (800 c.c.) at 70–80°. The solution

was just acidified to litmus, and the precipitated dihydroxyquinoline collected (Found : N, 8.7. Calc. : N, 8.7%).

Further addition of acid to the filtrate precipitated acetylanthranilic acid in a crystalline condition.

4(or 2)-*Hydroxy-2(or 4)-acetoxyquinoline* was obtained when 2 : 4-dihydroxyquinoline (1 g.) was heated with acetic anhydride (20 c.c.) and three drops of pyridine on the steam-bath for  $\frac{3}{4}$  hour. The derivative crystallised from alcohol in needles, m. p. 214—215° (Found : C, 65.1; H, 4.5; N, 6.6.  $C_{11}H_9O_3N$  requires C, 65.0; H, 4.5; N, 6.9%), readily soluble in acetic acid and acetone, moderately readily soluble in methyl alcohol, chloroform, ethyl acetate, and benzene, sparingly soluble in ether and light petroleum.

4(or 2)-*Hydroxy-2(or 4)-p-nitrobenzyloxyquinoline* possesses similar solubility properties and was prepared by refluxing a mixture of 2 : 4-dihydroxyquinoline (4 g.), alcohol (250 c.c.), *p*-nitrobenzyl bromide (6 g.), and potassium hydroxide (2 g.) for 2 hours. Yellow crystals separated from the filtered solution, and this substance crystallised from alcohol in pale yellow plates, m. p. 247° (decomp.) (Found : C, 64.8; H, 4.3; N, 9.7.  $C_{16}H_{12}O_4N_2$  requires C, 64.9; H, 4.1; N, 9.5%).

3-Nitro-2 : 4-dihydroxyquinoline (I) was prepared by Gabriel's method (*Ber.*, 1918, 51, 1500) in 85% yield, and also by nitration in sulphuric acid solution in somewhat inferior yield. A clear proof of the constitution of this derivative does not appear to have been recorded, but we have now observed that a small amount of aniline is formed on distillation with soda-lime.

The *monoacetyl* derivative was obtained under the conditions described above for the acetylation of 2 : 4-dihydroxyquinoline. It formed yellow needles, m. p. 194° (decomp.), from alcohol (Found : C, 53.6; H, 3.6; N, 11.1.  $C_{11}H_8O_5N_2$  requires C, 53.2; H, 3.3; N, 11.3%).

Attempts to obtain a methyl ether of 2 : 4-dihydroxyquinoline were unsuccessful, but the action of diazomethane was not tried.

3 : 6-Dinitro-2 : 4-dihydroxyquinoline (II).—Powdered potassium nitrate (16 g.) was added during 1 hour to a solution of 2 : 4-dihydroxyquinoline (10 g.) in sulphuric acid (100 c.c.) with stirring and cooling to below 5°. Nitric acid (20 c.c.) was then introduced in four portions, and the stirring continued at room temperature for 2½ hours. The brown liquid was added to crushed ice, and the yellow solid isolated and dissolved in hot aqueous sodium carbonate. On cooling, the *sodium* salt separated in glistening, slender, yellow needles (Found : Na, 8.2.  $C_9H_4O_6N_3Na$  requires Na, 8.4%). The regenerated nitrophenol was almost colourless and crystallised from acetic acid in long needles, m. p. 200° (decomp.) (yield, 60%)



(Found: C, 43.5; H, 2.2; N, 16.8.  $C_9H_5O_6N_3$  requires C, 43.1; H, 2.0; N, 16.7%).

3 : 6-Dinitro-2 : 4-dihydroxyquinoline is moderately readily soluble in the simple alcohols, acetone and hot water, but is very sparingly soluble in ether, light petroleum, benzene, ethyl acetate, and chloroform. It does not dissolve readily in cold aqueous sodium carbonate, but with sodium hydroxide an orange-red disodium salt is produced. The stability of this substance towards alkali is remarkable; 1 gram was heated with 15 c.c. of 10% sodium hydroxide solution in a sealed tube at 145° for 10 hours without suffering any decomposition.

A completely reduced acid solution became deep blue, quickly changing to reddish-brown, on the addition of ferric chloride.

The *monoacetyl* derivative was obtained by heating a mixture of the dinitrodihydroxyquinoline (1 g.) and acetic anhydride (20 c.c.), with stirring, just to the boiling point. The yellow solution deposited almost colourless plates, m. p. 190° (decomp.) after recrystallisation from acetic acid (Found: C, 45.3; H, 2.6; N, 14.2.  $C_{11}H_7O_7N_3$  requires C, 44.9; H, 2.4; N, 14.3%).

3 : 6 : 8-Trinitro-2 : 4-dihydroxyquinoline (III).—Finely powdered potassium nitrate (11 g.) was gradually added with shaking to a solution of 3 : 6-dinitrohydroxyacetoxyquinoline (5 g.) in 10% oleum (50 c.c.), and the yellow liquid stirred at 85° for 3 hours and then at 90—95° for 4 hours, the temperature having been raised very gradually. The product was slowly added to water (200 c.c.) with stirring. The pale brown solid obtained crystallised from acetic acid in pale yellow leaflets, m. p. 192—193° (decomp.) (yield, 65%) (Found: C, 36.9; H, 1.6; N, 18.4.  $C_9H_4O_8N_4$  requires C, 36.6; H, 1.4; N, 18.9%).

This *trinitrodihydroxyquinoline* is fairly readily soluble in water, alcohol and ethyl acetate and readily soluble in acetone; it is sparingly soluble in most other organic solvents.

The solution in aqueous sodium carbonate is golden-yellow. In aqueous sodium hydroxide the compound gives a deep yellow solution, from which a sparingly soluble sodium salt separates almost immediately; there is no change on boiling: this behaviour is in marked contrast with that of trinitrostrychnol.

The *monoacetyl* derivative was prepared by heating the trinitrodihydroxyquinoline with acetic anhydride for 5 minutes; it crystallised in colourless elongated plates, m. p. 158° (decomp.) (Found: C, 38.8; H, 1.9.  $C_{11}H_6O_9N_4$  requires C, 39.1; H, 1.8%).

The oxidation and nitration of the trinitrodihydroxyquinoline (1 g.) afforded a proof of its constitution and was effected by heating the substance with a mixture of acetic acid (10 c.c.) and nitric acid (10 c.c., *d* 1.5) for  $\frac{1}{2}$  hour on the steam-bath and, after addition of

water (10 c.c.), refluxing the solution for  $\frac{1}{2}$  hour and concentrating it to a syrup. The picric acid formed was isolated as its sodium salt and characterised by its m. p., undepressed by admixture with an authentic specimen, and by other properties.

**2-Chloro-3:5-dinitrobenzoyl Chloride.**—2-Chloro-3:5-dinitrobenzoic acid (Purgotti and Contardi, *Gazzetta*, 1902, **32**, i, 526) was treated with phosphorus pentachloride; the *chloride* (mentioned by Barnett, *Ber.*, 1925, **58**, 1610, without properties or analysis) crystallised from ether-benzene in white needles, m. p.  $62^{\circ}$  (Found: Cl, 26.7.  $C_7H_2O_5N_2Cl_2$  requires Cl, 26.8%). Attempts to condense the chloride with ethyl sodioacetoacetate and to hydrolyse the product were fruitless.

**3:5-Dinitro-2-methoxybenzoyl Chloride.**—The acid was obtained in 85% yield by following Ullmann's directions (*Annalen*, 1909, **366**, 85), and in 95% yield by nitrating *o*-methoxybenzoic acid (20 g.) with a mixture of sulphuric acid (100 c.c.) and nitric acid (30 c.c., *d* 1.5) for  $\frac{1}{2}$  hour at room temperature.

The *chloride* crystallised in plates when the crude product was washed with light petroleum; it had m. p.  $37-38^{\circ}$  (Found: Cl, 13.8.  $C_8H_5O_6N_2Cl$  requires Cl, 13.6%). Condensations with the sodium derivatives of ethyl acetoacetate and ethyl malonate led to no satisfactory outcome.

**Methyl 3:5-Dinitro-2-acetamidobenzoate.**—Salkowski (*Annalen*, 1874, **173**, 46) obtained methyl 3:5-dinitroanthranilate by the action of ammonia on methyl dinitroethoxybenzoate, and recorded the m. p.  $166^{\circ}$ . Esterification of 3:5-dinitroanthranilic acid (Purgotti and Contardi, *loc. cit.*) by means of 5% methyl-alcoholic sulphuric acid gave the same derivative, m. p.  $165-166^{\circ}$ , in 71% yield (Found: C, 39.6; H, 3.1. Calc. for  $C_8H_7O_6N_3$ : C, 39.8; H, 2.9%). The corresponding ethyl ester had m. p.  $136^{\circ}$ .

Acetylation of the methyl ester (2.5 g.) was carried out by means of acetic anhydride (25 c.c.) and a drop of sulphuric acid. The *acetyl* derivative crystallised from the solution after a few minutes and separated from benzene in long colourless rods, m. p.  $172-173^{\circ}$  (Found: C, 42.3; H, 3.4.  $C_{10}H_9O_7N_3$  requires C, 42.4; H, 3.2%). The related *ethyl* ester could be obtained by the use of acetic anhydride without a catalyst; it crystallised from benzene in clusters of needles, m. p.  $174^{\circ}$  (Found: C, 44.9; H, 3.7; N, 14.2.  $C_{11}H_{11}O_7N_3$  requires C, 44.5; H, 3.7; N, 14.1%). Ring closure of these esters was attempted under a variety of conditions, but it could not be effected and thus a long series of attempts to prepare 6:8-dinitro-2:4-dihydroxyquinoline failed.

**6:8-Dinitro-2:5-dihydroxyquinoline (IV).**—5-Aminocarbostyryl has been prepared by Claus and Setzer (*J. pr. Chem.*, 1896, **53**, 392),

but the method was modified in some details. 5-Nitrocarbostyryl (10 g.) was mixed with hydrated stannous chloride (36 g.) and concentrated hydrochloric acid (70 g.). After boiling for a few minutes, the solution was concentrated, then diluted, and tin eliminated as sulphide. The filtrate was again concentrated until crystals separated from the hot liquid. After cooling and keeping, the hydrochloride was isolated (6.5 g.); it crystallised in long colourless rods and gave a deep brownish-red coloration with ferric chloride in aqueous solution.

Sodium nitrite (4 g.), dissolved in water (10 c.c.), was gradually added to a stirred solution and suspension of 5-aminocarbostyryl hydrochloride (9 g.) in water (100 c.c.) and nitric acid (20 c.c.,  $d$  1.42) cooled to  $0^{\circ}$ . The mixture was kept at  $0^{\circ}$  for 1 hour and then heated on the steam-bath for 2 hours; nitrogen was evolved at about  $70^{\circ}$ . An almost black, resinous substance which separated was collected and dissolved in acetic acid; the solution deposited crystals and, after several recrystallisations, 6 : 8-dinitro-2 : 5-dihydroxyquinoline was obtained in pale yellowish-brown prisms, m. p.  $260^{\circ}$  (decomp.). A small additional amount was obtained from the reaction mother-liquor and had m. p.  $261^{\circ}$  (decomp.) (Found : C, 43.2; H, 2.3.  $C_9H_5O_6N_3$  requires C, 43.0; H, 2.0%). The substance is moderately readily soluble in alcohol, acetone, ethyl acetate, and water and sparingly soluble in chloroform, benzene, ether, and light petroleum. The aqueous solution is golden-yellow, and the solution in cold aqueous sodium carbonate is yellow. With aqueous sodium hydroxide, a deep red salt is produced; this dissolves to an orange-red solution on heating.

When the substance was refluxed with fifteen times its weight of nitric acid ( $d$  1.5) for 3 hours, a small amount of styphnic acid, m. p.  $175^{\circ}$ , was produced.

The reduced acid solution is not fluorescent and develops a bright red colour on the addition of ferric chloride.

The derivative obtained on acetylation with boiling acetic anhydride for 10 minutes crystallised from alcohol in clusters of very pale yellow needles, m. p.  $178^{\circ}$ .

6 : 8-Dinitro-2 : 7-dihydroxyquinoline (V).—Decker (*J. pr. Chem.*, 1901, 64, 99) recorded meagre details of his preparation of 7-nitrocarbostyryl and did not state the yield. Following his method as closely as possible, we found this to be 23% : under the following conditions, the yield is about 60%.

A solution of 7-nitroquinoline (22 g.) in water (1600 c.c.), boric acid (160 g.), and sulphuric acid (5 c.c.) was added to water (4400 c.c.) and heated on the steam-bath until a clear solution resulted. Fresh bleaching powder (200 g.) was digested with water (900 c.c.)

for 24 hours, and the filtered solution added to the nitroquinoline solution. After 24 hours, the precipitate was collected and boiled for 5 minutes with a solution of sodium hydroxide (14 g.) in water (1100 c.c.). Acidification of the alkaline filtrate afforded a voluminous precipitate of the carbostyryl. The reduction was carried out like that of the isomeride (above), and the diazotisation, decomposition and simultaneous nitration were also similar to those already described. Here, however, the black resin yielded nothing, and the filtrate from it, after being heated for a further period, was cooled and kept. The yellow solid that separated was collected, washed, and dried; it then crystallised from benzene in glistening yellow plates that gradually darkened on heating and had m. p. 207—208° (decomp.), exploding a few degrees higher. The results of analyses indicated a composition midway between that of a mono- and of a di-nitro-derivative. Accordingly, the product (1 g.) was dissolved in sulphuric acid (5 c.c.), and potassium nitrate (2 g.) added slowly with stirring. The mixture was poured into water (25 c.c.), and the precipitate crystallised several times from aqueous acetic acid, giving glistening, pale orange parallelepipeds, which darkened on heating but did not melt below 310°. At higher temperatures, explosion occurred, and for this reason no analysis by combustion could be performed. By using a very large excess of copper oxide, a Pregl-Dumas estimation of nitrogen could be carried out (Found : N, 16.6.  $C_9H_5O_6N_3$  requires N, 16.7%).

The substance is soluble in hot water to a yellow solution, and in this respect and in other solubility properties and colour reactions with alkalis it resembles the dinitro-2:5-dihydroxyquinoline described above.

The decomposition to styphnic acid was more facile than with the isomeride and could be effected by boiling the substance (0.5 g.) under reflux with nitric acid (5 c.c., *d* 1.5), acetic acid (5 c.c.), and water (5 c.c.) for  $\frac{1}{2}$  hour. The liquid was evaporated to dryness, and the residue extracted with ether; the resulting styphnic acid had m. p. 174—175°. This treatment does not change dinitro-2:5-dihydroxyquinoline to any appreciable extent.

*3-Nitroanisic Acid and Derivatives.*—The conditions for the nitration of *p*-tolyl carbonate (D.R.-P. 206,638) were modified.

A mixture of nitric acid (102 g., *d* 1.5) and sulphuric acid (265 g.) was gradually added to a stirred solution of *p*-tolyl carbonate (181 g.) in sulphuric acid (1200 c.c.) kept below 20°. After 5 hours, the product was isolated and hydrolysed; the yield of the nitro-cresol was 75%.

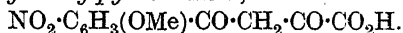
3-Nitroanisic acid has been obtained by Simonsen and Rau (J., 1917, 111, 235) by a series of reactions from 2-nitroanisic acid.

It can also be prepared by oxidation of 2-nitro-*p*-tolyl methyl ether in 35% yield. 2-Nitro-*p*-tolyl methyl ether (100 g.) was refluxed with a solution of potassium permanganate (120 g.) in water (2500 g.), further quantities of permanganate (180 g.) being introduced in the course of 5 hours and the boiling continued for 2 hours more. The acid, isolated in the known manner, crystallised from acetic acid in white hexagonal prisms, m. p. 195—196° (Found: C, 48.6; H, 3.9. Calc. for  $C_8H_7O_5N$ : C, 48.7; H, 3.6%).

Hydrogen chloride was the catalyst used in the preparation of the *ethyl ester*, which crystallised from alcohol in colourless plates, m. p. 71—72° (Found: C, 53.2; H, 5.0.  $C_{10}H_{11}O_5N$  requires C, 53.3; H, 4.9%).

The *chloride* was obtained by boiling the acid (50 g.) for 3 hours with pure thionyl chloride (140 c.c.). The yield was 53 g. and the derivative crystallised from light petroleum in small white tablets, m. p. 56° (Found: C, 44.3; H, 2.9.  $C_8H_6O_4NCl$  requires C, 44.5; H, 2.8%).

*2-Nitro-4-methoxybenzoylpyruvic Acid,*



—2-Nitroanisoyl chloride was brought into reaction with an equimolecular quantity of ethyl sodioacetoacetate in dry ethereal solution and suspension; the mixture was refluxed for 1 hour. The oily product gave a *potassium* salt which crystallised from alcohol in bright yellow leaflets (Found: K, 11.0.  $C_{14}H_{14}O_7NK$  requires K, 11.2%). The regenerated ester (25 g.) was refluxed for 8 hours with a mixture of sulphuric acid (50 g.) and water (100 c.c.), and about 6 g. of 2-nitro-4-methoxyacetophenone were isolated from the mixture as a yellowish-brown oil. This ketone (5 g.) and then ethyl oxalate (7 g.) were added with shaking and cooling to a solution of sodium (3 g.) in alcohol (100 c.c.). After 24 hours, water (500 c.c.) was introduced, and the filtered liquid acidified with hydrochloric acid. On keeping, a pale brown, flocculent substance was deposited which crystallised from benzene—light petroleum in almost colourless, feathery needles, m. p. 161° (yield, 65%) (Found: C, 49.4; H, 3.6.  $C_{11}H_9O_7N$  requires C, 49.4; H, 3.4%).

The *acid* is readily soluble in most organic solvents with the exception of light petroleum. It gives a bright yellow solution in aqueous sodium hydroxide and a deep reddish-brown ferric chloride reaction in alcoholic solution. Reduction with alkaline hydro-sulphite, followed by oxidation, gave a bluish-green precipitate of dimethoxyindigotin.

*4-Hydroxy-7-methoxyquinoline-2-carboxylic Acid* (7-Methoxykynurenic Acid) (VI).—A hot solution of crystallised ferrous sulphate (40 g.) in water (80 c.c.) was slowly added to one of 2-nitro-4-meth-

oxybenzoylpyruvic acid (10 g.) in water (100 c.c.) and aqueous ammonia (60 c.c.,  $d$  0.880). The liquid was heated for  $\frac{1}{2}$  hour on the steam-bath and filtered hot, and the precipitate washed with boiling dilute aqueous sodium carbonate. The combined filtrates were acidified, and the whole process was repeated on the isolated solid. The crude acid was boiled with acetic acid (50 c.c.), and the residue crystallised from a much larger volume of the same solvent, affording microscopic needles (2 g.), m. p.  $278^{\circ}$  (decomp.) (Found: C, 60.0; H, 3.8.  $C_{11}H_9O_4N$  requires C, 60.3; H, 4.1%). The acid is extremely sparingly soluble in the usual organic solvents. Its solution in sulphuric acid is yellow, and in alkaline solution it couples with benzenediazonium chloride to a red azo-compound.

*3(or 8)-Nitro-7-methoxykynurenic Acid.*—A solution of 7-methoxykynurenic acid (0.5 g.) in nitric acid (5 c.c.,  $d$  1.5) was stirred for 15 minutes, heated at  $30^{\circ}$  for 10 minutes, cooled, and poured into water. The derivative crystallised from acetic acid in clusters of almost colourless needles, m. p.  $250^{\circ}$  (decomp.) (Found: N, 10.5; MeO, 11.3.  $C_{11}H_8O_6N_2$  requires N, 10.6; 1MeO, 11.7%). The acid is soluble in alcohol, moderately readily soluble in acetone, chloroform and ether, and very sparingly soluble in other organic solvents of low b. p. It gives bright yellow alkaline solutions.

*3 : 6 : 8-Trinitro-7-methoxykynurenic Acid.*—A solution of 7-methoxykynurenic acid (0.5 g.) in nitric acid (5 c.c.,  $d$  1.5) was refluxed for 1 hour and then evaporated to dryness on the steam-bath; the residue crystallised from acetic acid in colourless, nearly rectangular prisms, which darkened but did not melt below  $310^{\circ}$  (Found: N, 15.8; MeO, 8.8.  $C_{11}H_6O_{10}N_4$  requires N, 15.8; 1MeO, 8.8%). This *trinitromethoxykynurenic acid* is moderately readily soluble in alcohol, acetone, or ethyl acetate, but is almost insoluble in other usual solvents. The solution in aqueous sodium carbonate is pale yellow, and the yellow solution in cold aqueous sodium hydroxide almost immediately deposits a yellow sodium salt.

A number of experiments were made on the exhaustive nitration of decarboxylated 7-methoxykynurenic acid and specimens undoubtedly containing 3 : 6 : 8-trinitro-7-methoxyquinoline were obtained. These did not show the characteristic behaviour of trinitrostrychol towards hot aqueous sodium hydroxide, and we are convinced that the trinitro-4 : 7-dihydroxyquinoline derivatives are more stable than trinitrostrychol.

*6-Nitrosalicylaldehyde (VII).*—Chloroform (24 c.c.) was added to a solution of *m*-nitrophenol (30 g.) in water (200 c.c.) and sodium hydroxide (40 g.), and the mixture refluxed for 1 hour. After removal of the excess of chloroform, the solution was acidified with sulphuric acid and distilled in steam. The pale yellow solid (yield,

3%) in the distillate crystallised from light petroleum or methyl alcohol in pale yellow prisms, m. p. 54–55° (Found: N, 8.6.  $C_7H_5O_4N$  requires N, 8.4%). The sodium salt was orange-red, and the ferric chloride coloration in alcoholic solution was reddish-brown. The salicylaldehyde configuration was confirmed by applying Dakin's reaction, a substance giving pyrocatechol-type reactions being obtained in small yield.

Methylation by means of methyl sulphate and sodium hydroxide yielded the *methyl* ether, which crystallised from carbon tetrachloride in colourless plates or needles, m. p. 111° (Found: C, 52.9; H, 3.9.  $C_8H_7O_4N$  requires C, 53.0; H, 3.9%). This methoxy-*o*-nitrobenzaldehyde gave a bulky, deep blue precipitate of dimethoxyindigotin (dark brownish-purple lustre) when cold aqueous sodium hydroxide was added to its solution in acetone.

THE UNIVERSITIES OF OXFORD AND MANCHESTER (1925).

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### LIII.—*The Reaction between Cupric Chloride and Hydrazine Sulphate.*

By THOMAS IREDALE and CATHERINE ELEANOR MALLEN.

DOUBLE compounds of the salts of hydrazine and copper, both cuprous and cupric, have been described (Curtius and Jay, *J. pr. Chem.*, 1894, **50**, 311; Hofmann and Marburg, *Annalen*, 1899, **305**, 191, 222; Ranfaldi, *Atti R. Accad. Lincei*, 1906, **15**, ii, 95; Franzen and Lucking, *Z. anorg. Chem.*, 1911, **70**, 152; Ferratini, *Gazzetta*, 1912, **42**, i, 138), and copper salts have been used for the gasometric estimation of hydrazine (Purgotti, *ibid.*, 1896, **26**, 559; de Girard and de Saporta, *Bull. Soc. chim.*, 1904, **31**, 905; Rimini, *Atti R. Accad. Lincei*, 1905, **14**, i, 386; Ebler, *Z. anorg. Chem.*, 1905, **47**, 371). The cupric double compounds are usually formed without any chemical action other than perhaps a double decomposition. This is possible as a rule only in neutral or somewhat acid solutions; in alkaline solutions reduction to a cuprous salt, finally giving cuprous oxide, takes place, with evolution of nitrogen:  $8Cu^{++} + 2N_2H_5^+ + 10OH^- = 8Cu^+ + 10H_2O + 2N_2$ . According to Gutbier (*Z. anorg. Chem.*, 1902, **32**, 355), colloidal cuprous oxide may sometimes be formed in this way under certain conditions; with high concentrations of hydrazine, however, copper itself may be the final reduction product (Rimini, *loc. cit.*; Curtius and Jay, *Ber.*, 1887, **20**, 1632). Brown, amorphous solids of uncertain composition are sometimes precipitated which deposit copper on standing. On exposure to air they form basic copper carbonates.

By working under certain conditions, we have prepared from hydrazine sulphate and cupric chloride a new *compound* which is more complex than any hitherto described, and has some unusual properties.

#### EXPERIMENTAL.

*N*-Cupric chloride solution is run drop by drop into a mixture of 40 g. of hydrazine sulphate in 250 c.c. of water with 25 g. of potassium hydroxide (or the equivalent sodium hydroxide) in 250 c.c. of water. The solution turns blue at first, and then becomes brown, with evolution of nitrogen. A brown precipitate begins to form, and if the cupric chloride is run in slowly, a stage is reached where glistening brown plates separate. Further quantities of the chloride should be added cautiously in order to avoid formation of a blue solution due to excess of copper salt. The crystals are allowed to settle, filtered off as rapidly as possible on a Buchner funnel, washed with 95% alcohol and finally with absolute alcohol, kept over sulphuric acid in a vacuum desiccator, and analysed without further purification.

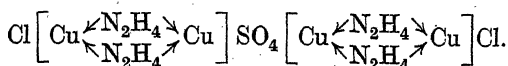
*Analysis.* (i) From the solution in hydrochloric acid, hydrogen sulphide precipitated copper sulphide; this was dissolved in nitric acid, and the metal estimated by the iodide method. (ii) The filtrate from the sulphide was freed from excess of hydrogen sulphide by a current of carbon dioxide, and the hydrazine was estimated in the solution by the iodine-bicarbonate method. (iii) Chlorine was estimated either by direct weighing as silver chloride, or by the Volhard method after an ammoniacal solution of the compound had been acidified with nitric acid. (iv) Sulphate was estimated as barium salt in the original hydrochloric acid solution (Found: Cu, 46.4; Cl, 12.1;  $N_2H_4$ , 21.1;  $SO_4$ , 18.0.  $2CuCl \cdot Cu_2SO_4 \cdot 4N_2H_4$  requires Cu, 46.3; Cl, 12.9;  $N_2H_4$ , 23.3;  $SO_4$ , 17.5%).

*Properties.* The *substance* is readily decomposed by cold water, but can be preserved for some time under anhydrous conditions. Hot water precipitates cuprous oxide, leaving a nearly neutral (methyl-orange) solution of hydrazine sulphate and chloride. The complex is insoluble in alcohol and in most organic solvents, but dissolves in formamide and pyridine to give straw-coloured solutions which rapidly become blue owing to oxidation; it also gives a similar solution in concentrated aqueous ammonia in an inert atmosphere, but access of oxygen rapidly produces the blue solution characteristic of cupric complexes. This rapid oxidation makes satisfactory recrystallisation from formamide difficult. Dilute sulphuric or nitric acid causes precipitation of copper, but hydrochloric acid at first yields a white precipitate which dissolves to a



colourless solution when the concentration of acid is increased, doubtless owing to the solubility of cuprous chloride in the concentrated acid.

The compound might simply be a double salt, but there appear to be at least three reasons for regarding it as fully co-ordinated: (1) the small number of acid radicals compared with hydrazine molecules and copper atoms; (2) the dark colour of the compound, probably indicating a large ion—the simpler double salts of cuprous copper are usually colourless, but the ammino-cuprous chlorides are brown (Lloyd, *J. Physical Chem.*, 1908, **12**, 398); (3) the ease with which it reacts with water to give cuprous oxide, suggesting the structure



Estimations of the molecular weight in pyridine and formamide were not satisfactory, owing to rapid oxidation and to the formation of other complexes.

Attempts to prepare related compounds have not been successful. When cupric sulphate is substituted for the chloride in the preparation, metallic copper separates.

We are indebted to Mr. W. J. Lawrence for checking some of the analyses.

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UNIVERSITY OF SYDNEY. [Received, November 28th, 1929.]

### LIV.—Nitration of Phenyl Substituents of Heterocyclic Nuclei.

By ROBERT FORSYTH and FRANK LEE PYMAN.

NITRATION of 2-phenylglyoxaline by addition of the nitrate of the base to cold sulphuric acid and heating at 100° gave 2-*p*-, 2-*o*-, and 2-*m*-nitrophenylglyoxalines in yields of 50, 1·5, and 0·2% of the theoretical respectively (Pyman and Stanley, *J.*, 1924, **125**, 2484). In view of the poor total yield, the nitration has now been repeated, the mixture, however, being kept for 60 hours at the ordinary temperature instead of being heated: the result was but little better, 2-*p*-nitrophenylglyoxaline being obtained in a yield of 57% of the theoretical, and oxidation of the by-products gave a mixture of acids from which crude *m*-nitrobenzoic acid was isolated in 5% yield. Attempts to obtain a clearer picture of a similar nitration by employing 2-phenyl-1-methylglyoxaline were unsuccessful, for the only identifiable products in this case were the *p*-nitro-derivative in

39% yield and *p*-nitrobenzoic acid (by oxidation of the by-products) in 4.4% yield.

Whilst the above nitrations yield *p*-nitro-derivatives as main products, the nitration of 2-phenylglyoxaline-4 : 5-dicarboxylic acid (Pyman and Stanley, *loc. cit.*), 2-phenyl-4 : 5-dihydroglyoxaline, and benzamidine (Forsyth, Nimkar, and Pyman, J., 1926, 800) have been shown to yield predominantly *m*-nitro-derivatives. In the hope of throwing light on this difference in substitution, the nitration of a number of allied compounds has been studied, but experimental difficulties prevented anything more than an incomplete picture of the nitration being obtained in each case. 4-Hydroxy-2-phenyl-6-methylpyrimidine gave 50% of the *m*-nitro-compound, and oxidation of the mother-liquor gave a further 7% of *m*-nitrobenzoic acid : it thus resembles benzamidine rather than 2-phenylglyoxaline. The nitration of phenylacetamidine gave 75% of the *p*-nitro-derivative, just as the nitration of  $\beta$ -phenylethylamine gives mainly the *p*-compound, and 1-phenylglyoxaline also gave the *p*-nitro-compound (58%). On nitration, 4-phenylpiperidine gave the *p*-, *o*-, and *m*-nitro-compounds in yields of 52, 8, and 3% respectively : the proportion of *m*-compound is thus considerably less than in the nitration of 4-phenylpyridine, where the *p*-, *o*-, and *m*-compounds were isolated in yields of 38, 13, and 28% respectively.

We regret that in publishing our paper on the nitration of 2-, 3-, and 4-phenylpyridines (J., 1926, 2912) we overlooked the previous publication of Tschitschibabin and Schemjakina (*J. Russ. Phys. Chem. Soc.*, 1921, 53, 217) owing to the fact that no reference was made to it in our *Abstracts*, although it was abstracted in the *Chem. Zentralblatt*, 1923, ii, 1024. These authors, using different methods from ours, separated from the products of interaction of pyridine with diazotised *p*-nitroaniline two *p*-nitrophenylpyridines, m. p. 131—131.5° and 146—147° respectively. They proved that the first was 2-*p*-nitrophenylpyridine (for which we found m. p. 130.5—131.5°) and assumed that the second was 4-*p*-nitrophenylpyridine. In view of our results, however, it is clear that their second compound was 3-*p*-nitrophenylpyridine, for which we found m. p. 148—149°.

#### EXPERIMENTAL.

*Nitration of 2-Phenyl-1-methylglyoxaline.*—2-Phenyl-1-methylglyoxaline nitrate, described as needles, m. p. about 100°, but not analysed by Balaban and King (J., 1925, 127, 2701), crystallises from dry acetone in prismatic needles, m. p. 126—127° (corr.). It is anhydrous, readily soluble in water, and fairly readily soluble in alcohol or acetone (Found : C, 54.2; H, 5.3; N, 19.1.  $C_{10}H_{10}N_2.HNO_3$  requires C, 54.3; H, 5.0; N, 19.0%).

This salt (5 g.) was added to sulphuric acid (10 c.c.) below 0° and the solution was kept for an hour, heated at 100° for another hour, and diluted with ice-water. The colourless crystals which separated (0.56 g.; m. p. 167—168°) were rejected, as was also an ether-extract of the solution (0.38 g. of gummy crystals). When the aqueous solution was basified with sodium hydroxide, pale yellow crystals separated (2.4 g.; m. p. 90—100°); chloroform extracted from the mother-liquor 1.21 g. of syrupy bases. The precipitated base was converted into nitrate, which was crystallised from alcohol, giving pure 2-*p*-nitrophenyl-1-methylglyoxaline nitrate (2.05 g.; m. p. 184—185° [corr.]; yield, 34.1%); the mother-liquors gave a further 4.8% yield of the same substance rather less pure, and after oxidation with permanganate a 4.4% yield of crude *p*-nitrobenzoic acid.

The above nitrate and the base, m. p. 117—118° (corr.), and picrate, m. p. 214—215° (corr.), prepared from it were shown by the mixed melting-point method to be identical with the base and its salts prepared by the methylation of 2-*p*-nitrophenylglyoxaline, for which Balaban and King (*loc. cit.*) give the m. p.'s (nitrate) 186° (base) 116.5°, and (picrate) 212° (all corr.).

*Phenylacetamidine Nitrate*.—Phenylacetiminoethyl ether hydrochloride was prepared by the method of Luckenbach (*Ber.*, 1884, 17, 1421) in 92% yield; it had m. p. 99—100° (corr.; efferv.) after sintering from 97°. Luckenbach gives m. p. 85° after softening at 60°. This salt was converted into crude phenylacetamidine hydrochloride by means of alcoholic ammonia (Luckenbach, *loc. cit.*) and thence into the nitrate by means of silver nitrate. Phenylacetamidine nitrate was thus obtained in 93% yield. It crystallises from water in large rhombic prisms, m. p. 168—169° (corr.). Bernton (*Arkiv Kemi Min. Geol.*, 1918, 7, 1) gives m. p. 166—167°, but does not give an analysis of this salt. It is moderately easily soluble in water and sparingly soluble in alcohol (Found: N, 21.6.  $C_8H_{10}N_2.HNO_3$  requires N, 21.3%).

*Nitration of Phenylacetamidine*.—Phenylacetamidine nitrate (5 g.) was added to sulphuric acid (10 c.c.) below 0°. The solution was kept for one hour, heated at 100° for 2 hours, cooled, and diluted with ice-water. On extraction with ether, only a trace of material was removed. The aqueous solution was mixed with sufficient aqueous barium chloride to remove sulphate ions, filtered from barium sulphate, and concentrated to small bulk. Since the hydrochlorides obtained did not crystallise, they were dissolved in water and mixed with the equivalent quantity of silver nitrate. After removal of silver chloride and concentration, crude *p*-nitrophenylacetamidine nitrate separated (5.66 g.; m. p. 150°); the mother-liquor gave on evaporation a sticky residue (0.59 g.; m. p. 100—115°). Crystal-

lisation of the nitrate of higher m. p. from alcohol gave pure *p*-nitrophenylacetamidine nitrate (4.42 g.; m. p. 157° [corr.]; yield, 69.7%), which was identified with the synthetic product described below by the mixed melting-point method. Attempts to fractionate the remaining material by crystallisation as nitrate, or as picrate, or after oxidation as nitrobenzoic acids, were fruitless. Orientation of *p*-nitrophenylacetamidine was effected by its synthesis from *p*-nitrophenylacetonitrile.

*Synthesis of p-Nitrophenylacetamidine.*—A suspension of *p*-nitrophenylacetonitrile (16.2 g.) in dry ether (20 c.c.) and absolute alcohol (4.6 g.) was saturated with dry hydrogen chloride. After 3 days, the *p*-nitrophenylacetiminoethyl ether hydrochloride, which had separated as a colourless crystalline powder, was collected and washed with ether (yield, 21.6 g.; 88%). When heated slowly from the ordinary temperature, it softened at about 188° and melted at 191–192° (corr.: decomp.), but it decomposed when placed in a bath at 150° (Found: Cl, 14.2.  $C_{10}H_{12}O_3N_2 \cdot HCl$  requires Cl, 14.5%). This salt is fairly readily soluble in alcohol, but sparingly soluble in ether; it is decomposed by water.

To *p*-nitrophenylacetiminoethyl ether hydrochloride (10 g.), suspended in absolute alcohol (10 c.c.), absolute alcohol saturated with ammonia at 0° was added gradually until a slight excess of ammonia remained after prolonged shaking. After being kept at 30° for 2 days, the mixture was diluted with water, acidified faintly with hydrochloric acid, concentrated to remove alcohol, and extracted with ether. The aqueous liquor was mixed with sufficient aqueous silver nitrate to remove chlorine ions, filtered from silver chloride, and concentrated. *p*-Nitrophenylacetamidine nitrate [7.6 g.; m. p. 157° (corr.)] then separated, and the mother-liquor on concentration gave a further deposit which, after removal of non-basic material by ether, afforded a further 0.72 g. of the nitrate, m. p. 157° (corr.). Total yield, 81%.

*p-Nitrophenylacetamidine nitrate* crystallises from water or moist alcohol in colourless coarse needles which rapidly become pale yellow in contact with air. It contains  $\frac{1}{2}H_2O$ , which is lost slowly over sulphuric acid, and the dried salt has m. p. 157° (corr.). It is moderately easily soluble in water or alcohol. Its aqueous solution becomes intensely red on addition of alkali (Found in air-dried salt: loss over  $H_2SO_4$ , 3.6.  $C_8H_9O_2N_3 \cdot HNO_3 \cdot \frac{1}{2}H_2O$  requires  $\frac{1}{2}H_2O$ , 3.6%. Found in dried salt: C, 39.8; H, 4.3; N, 22.9.  $C_8H_9O_2N_3 \cdot HNO_3$  requires C, 39.7; H, 4.1; N, 23.1%). The picrate crystallises from water or alcohol in yellow needles, m. p. 210° (corr.). It is very sparingly soluble in both these solvents, but fairly readily soluble in acetone.

*Nitration of 4-Hydroxy-2-phenyl-6-methylpyrimidine.*—The pyrimidine (5 g.) was added to sulphuric acid (10 c.c.) below 0°, followed gradually by potassium nitrate (2.7 g.). The mixture was kept for 2 hours at the ordinary temperature, heated for 2 hours at 100°, cooled, and poured into water; crude 4-hydroxy-2-*m*-nitrophenyl-6-methylpyrimidine then separated (4.02 g.; m. p. 245–247°). After prolonged fractional crystallisation, this product gave 3.1 g. (yield, 50%) of the pure base, m. p. 257° (corr.), and small quantities (in all, 7%) of crude *m*-nitrobenzoic acid were obtained by oxidising the bases isolated from the mother-liquors. Orientation of the main product was effected by its oxidation and comparison of the oxidation product with *m*-nitrobenzoic acid, and by its identification with 4-hydroxy-2-*m*-nitrophenyl-6-methylpyrimidine prepared from *m*-nitrobenzamidine and ethyl acetoacetate. The base so prepared by us had m. p. 257° (corr.); Pinner (*Ber.*, 1895, 28, 485) gives m. p. 254°.

*Nitration of 4-Phenylpiperidine.*—4-Phenylpiperidine was prepared by the reduction of 4-phenylpyridine with sodium and alcohol after Bailly (*Ber.*, 1887, 20, 2590), and the base, which distilled mainly at 264–267° (corr.)/756 mm. (Bailly gives b. p. 255–257°/725 mm.), was converted into nitrate, the yield of pure nitrate being 67% of the theoretical calculated on the 4-phenylpyridine employed. 4-Phenylpiperidine nitrate crystallises readily from water in colourless, diamond-shaped, anhydrous plates, m. p. 139° (corr.) (Found: C, 58.8; H, 7.1.  $C_{11}H_{15}N, HNO_3$  requires C, 58.9; H, 7.1%).

4-Phenylpiperidine nitrate (30 g.) was added to concentrated sulphuric acid (60 c.c.) cooled with water, and the solution was heated for  $\frac{1}{2}$  hour at 100°. After being basified with sodium hydroxide, the product was collected by ether and mixed with 5*N*-nitric acid (28 c.c.); a crystalline nitrate (24 g.; m. p. 140–145°) then separated. The mother-liquor was evaporated to dryness and the residue was mixed with absolute alcohol and kept; it then deposited an oil which became partly crystalline. This product was separated into crystalline and oily nitrates. All the crystalline nitrates were recrystallised several times from water (3–4 parts) and gave 16.4 g. of pure 4-*p*-nitrophenylpiperidine nitrate. The mother-liquors from this were mixed with sodium iodide and gave a mixture of hydriodides from which 4-*m*-nitrophenylpiperidine hydriodide separated first on crystallisation from water. The hydriodide mother-liquors were basified and extracted with ether and the recovered base was converted into nitrate, a little more of the pure *p*-salt being obtained; the mother-liquors then yielded with sodium iodide a mixture of hydriodides from which more of the *m*-salt was obtained. The oily nitrates mentioned above gave with

sodium iodide in aqueous solution an oily hydriodide, which became partly crystalline, and the crystalline part on recrystallisation from water gave 4-*o*-nitrophenylpiperidine hydriodide. The yields were *p*-nitrate, 19.42 g. pure (52.5%); *m*-hydriodide, 1.17 g. pure + 0.2 g. of m. p. 225° (3.1%); *o*-hydriodide, 3.8 g. pure air-dried (8.1%).

The three bases were precipitated by sodium hydroxide from aqueous solutions of their salts as oils, and when these were collected by ether the *p*- and *m*-bases crystallised, melting without further purification at 95° and 77° respectively, whereas the *o*-base did not crystallise. All three bases readily absorbed carbon dioxide from the air, yielding crystalline carbonates. On oxidation with permanganate the three bases gave the corresponding nitrobenzoic acids, which were identified by the mixed m. p. method.

4-*p*-Nitrophenylpiperidine nitrate crystallises from water in very pale buff plates, m. p. 162—163° (corr.), which are anhydrous and sparingly soluble in cold water (Found: C, 49.1; H, 5.7.  $C_{11}H_{14}O_2N_2.HNO_3$  requires C, 49.1; H, 5.6%). The hydriodide crystallises from alcohol in deep yellow, anhydrous prisms, m. p. 189—190° (corr.), which are sparingly soluble in cold water or alcohol (Found: C, 39.9; H, 4.5.  $C_{11}H_{14}O_2N_2.HI$  requires C, 39.5; H, 4.5%).

4-*m*-Nitrophenylpiperidine hydriodide crystallises from water in flat, pale yellow needles, m. p. 236° (corr.). It is anhydrous and sparingly soluble in cold water (Found: C, 39.6; H, 4.5.  $C_{11}H_{14}O_2N_2.HI$  requires C, 39.5; H, 4.5%). The nitrate crystallises from water in cream-coloured prismatic needles, m. p. 205—206° (corr.), which are sparingly soluble in cold water.

4-*o*-Nitrophenylpiperidine hydriodide crystallises from water in almost colourless prismatic needles, containing 1H<sub>2</sub>O, which are sparingly soluble in cold water. After drying at 100°, it melts at 160—161° (corr.) (Found in air-dried salt: loss at 100°, 5.1.  $C_{11}H_{14}O_2N_2.HI.H_2O$  requires H<sub>2</sub>O, 5.1%. Found in dried salt: C, 39.5; H, 4.5%). The nitrate crystallises from water in almost colourless prisms, m. p. 131—132° (corr.), which are more readily soluble in water than the nitrates of the *p*- and *m*-isomerides.

*Nitration of 1-Phenylglyoxaline.*—When 1-phenylglyoxaline was dissolved in a slight excess of 5*N*-nitric acid, a solution was obtained which did not crystallise, but after addition of an excess of concentrated nitric acid and concentration of the solution under diminished pressure over sulphuric acid and sodium hydroxide, 1-phenylglyoxaline dinitrate crystallised in large prisms, m. p. 82—86° (corr.) (Found: C, 40.0; H, 3.7.  $C_9H_8N_2.2HNO_3$  requires C, 40.0; H, 3.7%). This salt (3.5 g.) was added gradually to concentrated

sulphuric acid (7 c.c.), cooled with water. The solution was kept for 2 hours, diluted with water (50 c.c.), filtered from a colourless non-basic precipitate (0.12 g.), and basified with aqueous sodium hydroxide; brown crystals (1.85 g.; m. p.  $195^{\circ}$  after sintering earlier) were then collected. The mother-liquor on extraction with ether gave only 0.1 g. of a brown oil, which became partly crystalline, but was neglected. When the brown crystals were extracted with hot dilute hydrochloric acid, some resin remained undissolved; the solution, after treatment with charcoal, was basified, 1-*p*-nitrophenylglyoxaline (1.6 g.; m. p.  $198-200^{\circ}$  after previous sintering) being precipitated. After crystallisation from alcohol, this gave 1.42 g. of the pure base (yield, 58%).

1-*p*-Nitrophenylglyoxaline crystallises from alcohol in cream-coloured prismatic needles, m. p.  $204-205^{\circ}$  (corr.) (Found: C, 56.9; H, 3.9.  $C_9H_7O_2N_3$  requires C, 57.1; H, 3.7%). It is insoluble in water and sparingly soluble in cold alcohol. The hydrochloride crystallises from dilute hydrochloric acid in almost colourless, elongated, anhydrous prisms, m. p.  $293-294^{\circ}$  (corr.; decomp.) (Found: Cl, 15.7.  $C_9H_7O_2N_3.HCl$  requires Cl, 15.7%).

In order to determine the orientation of the nitro-group, the base (0.75 g.) and methyl sulphate (0.75 c.c.) were heated for a few minutes at  $100^{\circ}$ ; a crystalline methosulphate was then formed. This was decomposed by boiling with aqueous sodium hydroxide; the *p*-nitroaniline (0.45 g.; m. p.  $132^{\circ}$ ) that separated gave 0.15 g. of the pure base (m. p.  $148^{\circ}$ , alone or mixed with pure *p*-nitroaniline) after purification.

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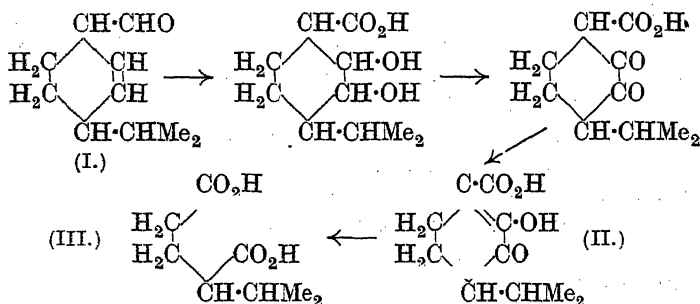
[Received, January 22nd, 1930.]

## LV.—The Constitution of Cryptal.

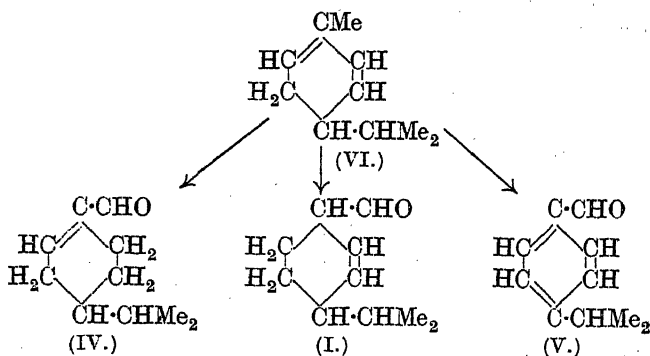
By ARTHUR RAMON PENFOLD and JOHN LIONEL SIMONSEN.

It was shown some years ago (Penfold, J., 1922, 121, 266) that the aldehyde "aromadendral" described by Smith (*J. Roy. Soc. New South Wales*, 1900, 34, 286; *Pharm. J.*, 1905, 75, 356, 382; *Trans. Roy. Soc. South Australia*, 1916, 40, 485) was a mixture of cumin-aldehyde, phellandral, and a new aldehyde, *l*-cryptal, isomeric with phellandral. This aldehyde has now been found to be 4-isopropyl- $\Delta^2$ -cyclohexenal (I), since on oxidation with potassium permanganate in acetone solution it gives *d*- $\alpha$ -isopropylglutaric acid (III) in almost quantitative yield, oxidation evidently proceeding in accordance

with the following scheme, diosphenolcarboxylic acid (II) being formed as an intermediate product :



A number of experiments were made with the object of oxidising *l*-cryptal to the corresponding *cyclohexenecarboxylic acid*, but these were uniformly unsuccessful. The reaction with silver oxide proceeds smoothly, but, under all the conditions employed, the acid was a gum which showed no tendency to crystallise. This was possibly due to its being a mixture of  $\alpha\beta$ - and  $\beta\gamma$ -isomerides, but the quantity of material available was insufficient for a separation to be attempted. In another series of experiments, *l*-cryptaloxime was treated with acetic anhydride with the object of converting it into the nitrile: the reaction, however, proceeded abnormally and, although a little impure nitrile was obtained, the main product was a crystalline substance, m. p. 102–103°, which from its analysis appeared to have the formula  $\text{C}_{22}\text{H}_{30}\text{O}_2\text{N}_2$  or  $\text{C}_{22}\text{H}_{32}\text{O}_2\text{N}_2$ . It had the properties of a weak base, but its constitution was not determined.



The constitution which is now shown to be that of *l*-cryptal was assigned originally by Wallach (*Annalen*, 1905, 340, 15; 343, 34) to the tetrahydrocuminaldehyde formed by the action of dilute sulphuric acid on  $\beta$ -phellandreneglycol. This aldehyde was shown subsequently to be identical with phellandral (4-isopropyl- $\Delta^1$ -cyclo-



hexenal) (IV) (compare Schimmel's Report, 1909, October, p. 88). The occurrence in admixture with each other of the three aldehydes cuminaldehyde (V), phellandral (IV), and cryptal (I), is not without biogenetic interest, since they can all three arise very simply from  $\alpha$ -phellandrene (VI), the chief hydrocarbon constituent of the oils in which they occur.

#### EXPERIMENTAL.

The *l*-cryptal used in these experiments was the original specimen prepared by Penfold in 1922.

*l*-Cryptaloxime was readily obtained by the interaction of an alcoholic solution of cryptal with hydroxylamine hydrochloride in the presence of sodium acetate. After distillation in steam the oxime was obtained as a thick oil, b. p.  $150^{\circ}/17$  mm.,  $n_D^{20}$  1.5139; it did not crystallise even when cooled to a low temperature (Found: C, 71.7; H, 9.8.  $C_{10}H_{17}ON$  requires C, 71.8; H, 10.2%).

When the oxime was mixed with an excess of acetic anhydride in the presence of sodium acetate, heat was generated and the solution became yellow. After 30 minutes' boiling, a very vigorous reaction occurred and the solution became deep brown. When the cooled solution was poured into water, a viscid brown oil separated: this was dissolved in ether, the extract washed with sodium carbonate solution, dried, and evaporated, and the residual oil distilled under diminished pressure; the greater part boiled at  $200$ – $210^{\circ}/23$  mm., leaving a considerable residue. The distillate, which smelt strongly of a nitrile, crystallised almost completely on keeping. The solid, after being drained on porous porcelain, crystallised from light petroleum (b. p.  $60$ – $80^{\circ}$ ) in fine long needles, m. p.  $102$ – $103^{\circ}$  (Found: C, 74.1, 74.3; H, 8.8, 8.6; N, 8.4.  $C_{22}H_{30}O_2N_2$  requires C, 74.6; H, 8.5; N, 7.9.  $C_{22}H_{32}O_2N_2$  requires C, 74.1; H, 9.0; N, 7.9%). This substance, which was optically inactive, was not attacked by alkali even on prolonged boiling; it was soluble in concentrated mineral acids and precipitated on dilution with water.

*l*-Cryptalphenylhydrazone is an oil, but the *p*-nitrophenylhydrazone crystallised from alcohol in terra-cotta, highly iridescent, soft needles, m. p.  $167^{\circ}$  (Found: N, 14.9.  $C_{16}H_{21}O_2N_3$  requires N, 14.6%).

*Oxidation of l*-Cryptal.—To the aldehyde (10 g.), dissolved in acetone (200 c.c.) and cooled to  $0^{\circ}$ , potassium permanganate (25 g.) was gradually added. The oxidation proceeded rapidly at first but later became very slow. Water (50 c.c.) was then added and the oxidation completed by the addition of potassium permanganate (20 g.). The manganese dioxide sludge was separated and well washed with boiling water and the filtrate was evaporated to a small bulk in a current of carbon dioxide. After acidification the oxid-

ation product was extracted with ether (10 times), the extract dried, and the solvent evaporated. The residual oil (11 g.) crystallised on keeping and after draining on porous porcelain had m. p. 90°. It was recrystallised from hydrochloric acid, yielding small glistening plates, m. p. 93—94°, of *d*- $\alpha$ -isopropylglutaric acid (Found : C, 55.2; H, 7.9; *M*, 175. Calc. : C, 55.1; H, 8.0%; *M*, 174). In aqueous solution (*c* = 0.766),  $[\alpha]_{5461} + 14.2^\circ$  was observed. The anhydride crystallised from light petroleum in the curious soft needles, resembling cotton-wool, described by Perkin (J., 1896, 69, 1495); the anilic acid had m. p. 154—155°.

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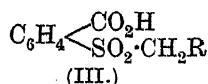
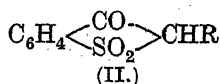
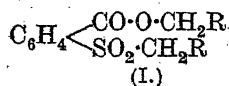
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## LVI.—Derivatives of 3-Keto-2 : 3-dihydrothionaphthen 1 : 1-Dioxide.

By AARON COHEN and SAMUEL SMILES.

CERTAIN members of this group were required in connexion with other experiments, but no systematic method of obtaining them was available. Treatment of 3-keto-2 : 3-dihydrothionaphthen with hydrogen peroxide gives the parent substance (II, R = H) in poor yield (Lanfry, *Compt. rend.*, 1912, 154, 1517), but the method is untrustworthy for the preparation of derivatives. Price and Smiles (J., 1928, 2860) prepared 3-keto-2-*p*-nitrophenyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide (II, R = *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>) from the sulphone ester (I, R = *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>) derived from *o*-carboxybenzenesulphonic acid, and the carbethoxy-derivative (II, R = CO<sub>2</sub>Et) was obtained in a similar manner.



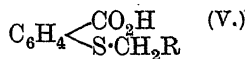
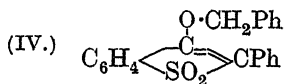
This mode of synthesis has now been further studied and, with certain limitations, has been found satisfactory; for instance, the *phenyl*, *o*-*nitrophenyl*, *acetyl*, and *benzoyl* derivatives (II, R = substituent) are readily obtained by reaction of the corresponding sulphone esters with sodium ethoxide.

The requisite sulphone esters (I) are often conveniently obtained in one operation from an alkali *o*-carboxybenzenesulphinate and the halogen derivative, but in cases (*e.g.*, I, R = Ph) where esterification does not proceed easily under the conditions it is more convenient to treat the ethyl ester of the sulphone acid (III) with sodium ethoxide,

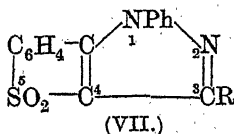
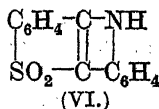
admixture of the product with the ether (*e.g.*, IV) thus being avoided.

The structural conditions necessary to this closing of the ring are provided by the sulphone group (compare Troeger and Kroseberg, *J. pr. Chem.*, 1913, **87**, 67) and by the nature of R. For instance, in contrast with the corresponding sulphones, the ester of the benzyl sulphide (V, R = Ph) does not yield the ketodihydrothionaphthen with sodium ethoxide (Apitzsch, *Ber.*, 1913, **46**, 3092), the ester of *o*-carboxyphenylmethylsulphone (I, R = H) does not give the cyclic sulphone, and the *ethyl* ester of *ethylene di-o-carboxyphenylsulphone* (as III, R = CH<sub>2</sub>·) is not converted into the dicyclic sulphone by this method.

The stability conferred on the thionaphthen ring by the substituents phenyl, acetyl, benzoyl, and nitrophenyl is remarkable; the derivatives having these substituents in the 2-position dissolve in warm aqueous alkali hydroxide without fission, whereas the parent substance is attacked by the cold reagent, yielding *o*-carboxyphenyl-methylsulphone.



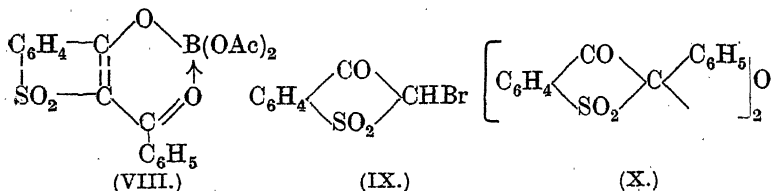
Very stable polycyclic systems are easily formed from derivatives of type (II): reduction of the *o*-nitrophenyl derivative leads directly to the *thionaphthindole dioxide* (VI), and the monophenyl-



hydrazones of the acetyl and benzoyl derivatives yield the thionaphthapyrazole dioxides (VII, R = Me and Ph, respectively).

The characters of 3-keto-2-benzoyl-2 : 3-dihydrothionaphthen and of the corresponding dioxide (II, R = CPh) have been contrasted in a few typical experiments: these indicate that the latter substance approaches more closely to the  $\beta$ -diketonic structure than the former, which behaves as a 2-hydroxy-ketone. For example, the thionaphthen is easily acetylated and yields only a monophenylhydrazone (Hart and Smiles, *J.*, 1924, **125**, 876), but the corresponding dioxide gives a *diphenylhydrazone* and cannot be acetylated under comparable conditions. The relationship is also well illustrated by the instability of the *borodiacetate* of the dioxide (VIII) in comparison with the stability of the characteristic derivative (VIII with S in place of SO<sub>2</sub>) of the thionaphthen. This relationship accords with

the observations of McClelland (J., 1929, 1590) that sulphur in the ortho-position to carbonyl favours enolisation of the latter by



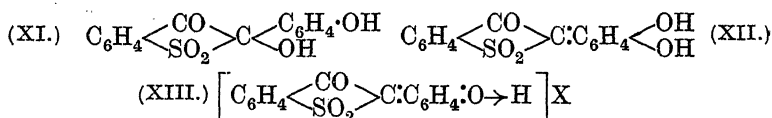
increasing the negative character of the oxygen, whereas conversion of the sulphide into the sulphone lessens the activity of the sulphur as a source of electrons and thus moderates the enolic tendency of the carbonyl oxygen.

The halogen derivatives of this series exhibit interesting features. Bromination proceeds easily at the 2-position when available hydrogen is present. The parent substance (II, R = H) yielded the 2:2-dibromo-derivative, and the monobromo-derivative (IX) could be obtained only by decomposition of the unstable 2-bromo-2-carbethoxy-compound (IX with CO<sub>2</sub>Et in place of H); other bromine derivatives of the 2-substituted ring (II with Br in place of H) were more stable.

In accordance with the known character of the sulphone group and with the observations of Macbeth and his co-workers (J., 1922, 121, 892, 904, 1116) on substances of analogous type, the halogen in the 2-bromo-derivatives is removed as hypobromite by alkali hydroxide, being replaced by hydrogen, except in the mono- and di-bromo-compounds, where the process is modified by fission of the sulphone ring system. Moreover, in the monobromo-derivatives (IX, and II with Br in place of H) the halogen quantitatively liberates iodine from potassium iodide. These reactions appear to be characteristic of chlorine or bromine in the 2-position. Nitrous acid also attacks hydrogen in this position: in the parent substance replacement is complete, the nitroso-derivative undergoing further substitution (compare Friedländer, *Ber.*, 1908, 41, 227), but with the 2-phenyl derivative oxidation ensues, the oxide (X) being formed. This oxide is devoid of basic character and the corresponding 2-bromo-derivatives do not exhibit the properties of salts.

These facts give useful information concerning the structure of the product obtained by the action of excess of nitrous acid on the 2-*p*-aminophenyl derivative. The red crystalline material thus formed is basic in character and the chloride, from which the base is regenerated by hydrolysis, furnishes a *ferrichloride* and a *chloroplatinate*. In composition the base conforms with the structure (XI), but this arrangement, which involves the association of

hydroxyl with the 2-carbon atom, cannot be adopted, since the 2-oxide is entirely lacking in basic character. Similarly, the association of halogen with the 2-position of the thionaphthen nucleus (XI with Cl in place of OH) cannot be admitted in the case of the chloride or bromide; these salts are merely hydrolysed by water or



dilute alkalis and do not exhibit the characteristic behaviour of the 2-bromo-derivatives (IX, and II with Br in place of H), which liberate hypobromite on treatment with such agents. Moreover, a quinolide structure (XII) similar to that proposed by Gomberg (*J. Amer. Chem. Soc.*, 1913, **35**, 1035) for one of the isomeric forms of 4-hydroxytriphenylcarbinol and analogous substances is unacceptable, since removal of water from the base in question is effected only with difficulty, prolonged heating in a vacuum in presence of phosphoric oxide being necessary. On the other hand, the formation and properties of the base and salts are well expressed by the formula XIII (X = OH or Cl) in which the kation is formed by co-ordination of hydrogen with the carbonyl group of the quinone. This view accords with those of Pfeiffer (*e.g.*, *Annalen*, 1917, **413**, 328) on the nature of salts formed by substances containing the carbonyl group.

#### EXPERIMENTAL.

**3-Keto-2-benzoyl-2 : 3-dihydrothionaphthen 1 : 1-Dioxide** (II, R = C<sub>6</sub>H<sub>5</sub>).—(a) A concentrated solution of  $\omega$ -bromoacetophenone (23 g.) was added to an alcoholic solution of *o*-carboxybenzenesulphonic acid (10 g.) (*J.*, 1928, 2860) which had been neutralised with concentrated aqueous potassium hydroxide. When the mixture was boiled, potassium bromide separated ( $\frac{1}{2}$  hour); the cooled liquid yielded a further quantity of this salt together with *phenacyl-o-carbophenacylphenylsulphone* (I, R = C<sub>6</sub>H<sub>5</sub>). This substance (70% yield) separated from acetone-alcohol in needles, m. p. 164° (Found : C, 65.1; H, 4.5; S, 7.5. C<sub>23</sub>H<sub>18</sub>O<sub>6</sub>S requires C, 65.4; H, 4.3; S, 7.6%). A solution of this ester (8 g.) in alcohol (50 c.c.) in which sodium (0.4 g.) had been dissolved was boiled for 30 minutes and the solvent was then evaporated after the addition of water. Benzoylcarbinol was removed by solution in ether and the aqueous liquid was mixed with an excess of dilute sulphuric acid. **3-Keto-2-benzoyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide**, which separated in 66% yield, crystallised from benzene in plates, m. p. 188° (Found : C, 62.6; H, 3.6; S, 11.0. C<sub>15</sub>H<sub>10</sub>O<sub>4</sub>S requires C, 62.9; H, 3.5; S, 11.2%).

(b) 3-Keto-2-benzoyl-2 : 3-dihydrothionaphthen (0.5 g.), suspended in acetic acid (10 c.c.) to which hydrogen peroxide (1 c.c. of 30%) had been added, dissolved after 2 days and the oxidation product, which was identical with the substance obtained as described above, separated.

The substance was recovered unchanged from 10% sodium hydroxide solution after 3 hours' boiling and attempts to obtain an acetyl or benzoyl derivative by the usual methods were unsuccessful. The *diphenylhydrazone*, m. p. 243° after crystallisation from alcohol, was obtained from the substance (1 mol.) and phenylhydrazine (3 mols.) in boiling concentrated benzene solution (Found : N, 12.2.  $C_{27}H_{22}O_2N_4S$  requires N, 12.0%).

When the preparation of a monophenylhydrazone of 3-keto-2-benzoyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide was attempted by boiling an alcoholic solution containing phenylhydrazine (1 mol.), 1 : 3-*diphenylthionaphthapyrazole* 5 : 5-dioxide (VII, R = Ph) was obtained : this crystallised from acetone in prisms, m. p. 225°, which were insoluble in alkali and responded to Knorr's pyrazole test (*Ber.*, 1893, 26, 100) (Found : N, 8.2; S, 8.8.  $C_{21}H_{14}O_2N_2S$  requires N, 7.8; S, 8.9%).

The *borodiacetate* (VIII) separated in lemon-yellow needles, m. p. 220° (decomp.), when a boiling solution of the substance (II, R = Ph) in acetic anhydride containing boroacetic anhydride was cooled. It was easily decomposed by cold water, yielding the parent substance (II); analysis was made by weighing this product (Found :  $C_{15}H_{10}O_4S$ , 68.9.  $C_{19}H_{15}O_6SB$  requires  $C_{15}H_{10}O_4S$ , 69.2%). For comparison, the *borodiacetate* of 3-keto-2-benzoyl-2 : 3-dihydrothionaphthen (VIII with S in place of  $SO_2$ ) was prepared in a similar manner : it formed red prisms which were very slowly decomposed by boiling water (Found :  $C_{15}H_{10}O_2S$ , 67.1.  $C_{19}H_{15}O_6SB$  requires  $C_{15}H_{10}O_2S$ , 66.7%).

3-Keto-2-phenyl-2 : 3-dihydrothionaphthen 1 : 1-Dioxide (II, R = Ph).—(a) Alcohol (50 c.c.) which contained benzyl chloride (6.8 g.) and the potassium salt of *o*-carboxybenzenesulphinic acid (14.2 g.) was boiled for 3 hours. When the potassium chloride had been removed, the sparingly soluble potassium salt (7.8 g.) of *o*-carboxyphenylbenzylsulphone (III, R = Ph) separated. The acid, liberated in the usual manner, crystallised from water in needles, m. p. 126—128° after dehydration at 100° (Found : C, 60.8; H, 4.3;  $H_2O$ , 6.2.  $C_{14}H_{12}O_4S.H_2O$  requires C, 61.1; H, 4.0;  $H_2O$ , 6.1%). The methyl ester (1 mol.), prepared from the silver salt, was heated for 20 minutes with alcohol which contained sodium ethoxide (1 mol.); the solvent was then evaporated, and an aqueous extract of the residue treated with an excess of dilute sulphuric acid. 3-Keto-2-phenyl-2 : 3-di-

*hydrothionaphthen 1 : 1-dioxide*, obtained in 60% yield, crystallised from acetone-alcohol in prisms, m. p.  $174^{\circ}$  (Found : C, 65.0; H, 3.9.  $C_{14}H_{10}O_3S$  requires C, 65.1; H, 3.9%). The yellow alkaline solution yielded unaltered material after 2 hours' boiling.

(b) This phenyl derivative was also obtained by boiling a solution of potassium *o*-carboxybenzenesulphinate (1 mol.) in alcohol which contained benzyl chloride (2 mols.) and treating the resulting solution with sodium ethoxide as usual. When the solvent and other volatile materials had been removed in steam, the remaining aqueous alkaline solution gave the 2-phenyl derivative in 15% yield on treatment with acid. An equal quantity of material which was insoluble in the alkali was identified with the *benzyl ether* (IV) of 3-hydroxy-2-phenylthionaphthen 1 : 1-dioxide synthesised from the 2-phenyl derivative (II, R = Ph) and benzyl chloride in alkaline solution : it separated from acetone-alcohol in prisms, m. p.  $146^{\circ}$  (Found : C, 72.4; H, 4.6; *M*, 357.  $C_{21}H_{16}O_3S$  requires C, 72.4; H, 4.6%; *M*, 348).

*3-Keto-2-acetyl-2 : 3-dihydrothionaphthen 1 : 1-Dioxide* (II, R = CO·CH<sub>3</sub>).—Alcohol (75 c.c.) which contained monochloroacetone (15 g.) and the potassium salt prepared from *o*-carboxybenzenesulphinic acid (15 g.) was boiled for 5 hours. The solution, which contained the sulphone ester (I, R = CO·CH<sub>3</sub>), was treated with sodium ethoxide in the usual manner. Half the volume of solvent was evaporated and the material which separated from the cooled residue was purified from water (charcoal). The required *product* was liberated from the aqueous solution by dilute mineral acid; it separated from benzene-ligroin in prisms, m. p.  $164^{\circ}$  (Found : C, 53.5; H, 3.7.  $C_{10}H_8O_4S$  requires C, 53.6; H, 3.6%). The ketone was recovered unchanged from a boiling alkaline solution. Attempts to prepare the substance by oxidation of 3-keto-2-acetyl-2 : 3-dihydrothionaphthen with hydrogen peroxide were unsuccessful, the chief product being "thioindigo."

The *monophenylhydrazone* was obtained by boiling an alcoholic solution of the ketone with phenylhydrazine (slightly more than 1 mol.) for 3 hours. It crystallised from alcohol in yellow needles, m. p.  $210^{\circ}$ , which were soluble in aqueous alkali (Found : C, 61.1; H, 4.8; N, 9.2.  $C_{16}H_{14}O_3N_2S$  requires C, 61.1; H, 4.8; N, 8.9%). When a solution of the phenylhydrazone in acetic acid containing a few drops of sulphuric acid was warmed at  $90^{\circ}$  for 1 hour, dehydration was effected and 1-phenyl-3-methylthionaphthapyrazole 5 : 5-dioxide (VII, R = CH<sub>3</sub>) was produced. This, isolated from the fluorescent solution by dilution, formed prisms, m. p.  $180^{\circ}$ , which were insoluble in alkali or acid (Found : N, 9.7.  $C_{16}H_{12}O_2N_2S$  requires N, 9.5%). The substance responded to Knorr's pyrazole test.

*3-Keto-2-o-nitrophenyl-2 : 3-dihydrothionaphthen 1 : 1-Dioxide* (II,  $R = o\text{-NO}_2\cdot\text{C}_6\text{H}_4$ ).—The *o*-nitrobenzyl ester (I,  $R = o\text{-NO}_2\cdot\text{C}_6\text{H}_4$ ) of *o*-carboxyphenyl-*o*-nitrobenzylsulphone was prepared from *o*-nitrobenzyl chloride and potassium *o*-carboxybenzenesulphinate in the usual manner; it separated from aqueous acetone in plates, m. p.  $156^\circ$  (Found: C, 55.1; H, 3.7; N, 5.9.  $\text{C}_{21}\text{H}_{16}\text{O}_8\text{N}_2\text{S}$  requires C, 55.3; H, 3.5; N, 6.1%). A solution of this substance (5 g.) in alcohol (100 c.c.) in which sodium (0.25 g.) had been dissolved was boiled ( $\frac{1}{2}$  hour); the solvent was then evaporated, and the residue treated with water and ether. The latter solvent removed *o*-nitrobenzyl alcohol. The aqueous solution on treatment with excess of dilute acid yielded *3-keto-2-o-nitrophenyl-2 : 3-dihydrothionaphthen dioxide* (2 g.), which crystallised from acetone in prisms, m. p.  $187^\circ$  (Found: C, 55.3; H, 3.2.  $\text{C}_{14}\text{H}_9\text{O}_5\text{NS}$  requires C, 55.5; H, 3.0%).

Zinc dust was added to a boiling solution of the nitro-compound in acetic acid. The product, separated from the cooled liquid and crystallised from alcohol, gave *thionaphthindole dioxide* (VI) in needles, m. p.  $220^\circ$  (Found: C, 65.6; H, 3.6; S, 12.4.  $\text{C}_{14}\text{H}_9\text{O}_2\text{NS}$  requires C, 65.9; H, 3.5; S, 12.6%). This substance was also prepared by oxidation of thionaphthindole obtained by McClelland in another manner (J., 1929, 1589).

*3-Keto-2-p-aminophenyl-2 : 3-dihydrothionaphthen 1 : 1-Dioxide* (II,  $R = p\text{-NH}_2\cdot\text{C}_6\text{H}_4$ ).—A concentrated aqueous solution of sodium hydrosulphite was added to a warm ( $70^\circ$ ) alkaline solution (200 c.c.) of the sodium salt (3 g.) of the 2-*p*-nitrophenyl derivative (J., 1928, 2862) until the red colour of the latter was discharged. When dilute acetic acid was added to the cooled mixture, the required amino-derivative (1.5 g.) was liberated. This separated from alcohol in yellow prisms, m. p. *ca.*  $180^\circ$ , which were too unstable for further purification. It was characterised by the *acetyl* derivative, which formed plates, m. p.  $226^\circ$ , from acetic acid (Found: C, 60.6; H, 4.3.  $\text{C}_{16}\text{H}_{13}\text{O}_4\text{NS}$  requires C, 60.9; H, 4.1%).

*Ethylenedi-o-carboxyphenylsulphone* (as III,  $R = \text{CH}_2$ ).—Alcohol (50 c.c.) which contained ethylene dibromide (5 g.) and the potassium salt derived from 10 g. of *o*-carboxybenzenesulphinic acid was boiled (4 hours). The solvent was then evaporated and ethylene dibromide was removed from the residue by a current of steam. The aqueous solution (charcoal) was mixed with excess of sulphuric acid (60%). The *product* liberated (40% yield) crystallised from acetone in needles, m. p.  $250^\circ$  (Found: C, 47.8; H, 3.7.  $\text{C}_{16}\text{H}_{14}\text{O}_8\text{S}_2$  requires C, 48.2; H, 3.5%). Boiling thionyl chloride converted it into the chloride, from which the *ethyl* ester was obtained in good yield. This formed plates from alcohol and had m. p.  $150^\circ$  (Found:



C, 52.7; H, 5.0; S, 14.2.  $C_{20}H_{22}O_8S_2$  requires C, 52.8; H, 4.8; S, 14.1%.

*2-Bromo-derivatives.*—These substances, except the monobromo-derivative of the parent compound, were obtained by the direct action of the necessary amount of bromine in a suitable solvent, usually acetic acid, and were isolated by dilution with water.

*2 : 2-Dibromo-3-keto-2 : 3-dihydrothionaphthen 1 : 1-dioxide* (IX with Br in place of H) crystallised from alcohol in needles, m. p. 148°. It liberated iodine from acidified aqueous potassium iodide. Halogen was determined in this manner (a) and also by the usual method (b) [Found : Br, (a) 47.2, (b) 47.1.  $C_8H_4O_3Br_2S$  requires Br, 47.1%]. The substance dissolved in warm aqueous alkali and the solution was found to contain carboxylic acids, evidently produced by rupture of the thionaphthen ring system.

*2-Bromo-3-keto-2 : 3-dihydrothionaphthen 1 : 1-dioxide* (IX). A suspension of the 2-carbethoxy-derivative (Feist, *Ber.*, 1925, 58, 2311) (2 g.) in acetic acid was heated together with a solution of bromine (1.4 g.) in the same solvent for 1½ hours, carbon dioxide being liberated. The product, isolated in the usual manner, crystallised from benzene in needles, m. p. 149–150° [Found : C, 36.9; H, 2.0; Br, (a) 30.7, (b) 30.2.  $C_8H_5O_3BrS$  requires C, 36.8; H, 1.9; Br, 30.6%]. It was decomposed by warm aqueous alkali, the ring suffering fission and bromine being eliminated.

*2-Bromo-3-keto-2-benzoyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide* (IX with CPh in place of H) crystallised from alcohol in needles, m. p. 168° (Found : Br, 22.1.  $C_{15}H_9O_4BrS$  requires Br, 21.9%). It dissolved in warm aqueous sodium acetate, and acid liberated the original 2-benzoyl compound from the solution.

*2-Bromo-3-keto-2-phenyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide* (IX with Ph in place of H) formed plates, m. p. 170°, from which aqueous sodium acetate removed halogen, replacing it by hydrogen (Found : Br, 23.7.  $C_{14}H_9O_3BrS$  requires Br, 23.8%).

*2-Bromo-3-keto-2-p-nitrophenyl-2 : 3-dihydrothionaphthen 1 : 1-dioxide* (as IX) formed plates, m. p. 155°, from acetic acid. The substance behaved in the usual manner with warm sodium acetate solution (Found : Br, 20.8.  $C_{14}H_8O_5NBrS$  requires Br, 20.9%). None of these bromine derivatives yielded perbromides or additive compounds with metallic bromides.

*The 2-Oxide of 3-Keto-2-phenyl-2 : 3-dihydrothionaphthen 1 : 1-Dioxide* (X).—(a) Concentrated hydrochloric acid (3 c.c.) was slowly added to alcohol (25 c.c.) which contained 3-keto-2-phenyl-2 : 3-dihydrothionaphthen dioxide (1 g.) and ethyl nitrite (2.7 c.c. of 15% solution) and the mixture was warmed at 90° for ¼ hour. The product (0.8 g.), obtained on cooling, separated from benzene, on

addition of light petroleum, as a microcrystalline powder, m. p.  $220^{\circ}$  (Found: C, 63.5; H, 3.7; *M*, 515.  $C_{28}H_{18}O_7S_2$  requires C, 63.4; H, 3.4%; *M*, 530).

(b) Chromic acid (0.25 g.) was added to acetic acid (15 c.c.) which contained the above phenyl derivative (1.1 g.), and the mixture was warmed and then diluted with water. After purification, the product (1 g.) was identified with that obtained in (a).

When 3-keto-2:3-dihydrothionaphthen 1:1-dioxide was treated with an excess of nitrous acid under similar conditions to the above, a substance was obtained in almost quantitative yield. It formed plates, which decomposed at  $173^{\circ}$ , and gave a red solution in cold aqueous alkali; in the warm reagent, decomposition took place, *o*-carboxybenzenesulphinic acid being formed (compare Friedländer, *loc. cit.*) (Found: C, 42.3; N, 9.4; S, 14.0.  $C_{16}H_9O_9N_3S_2$  requires C, 42.5; N, 9.3; S, 14.1%). From these data the substance appears to be a *nitroso-oximino* derivative containing the structure  $>C(NO) \cdot N(OH) \cdot C(NO)<$  formed by complete replacement of the 2-hydrogen atoms in the parent substance (II, R = H).

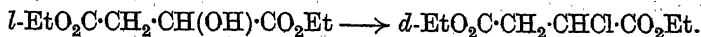
3-Keto-2-benzoyl-2:3-dihydrothionaphthen 1:1-dioxide was not attacked by nitrous acid.

3-Keto-2-*p*-quino-2:3-dihydrothionaphthen 1:1-Dioxide Hydroxide (XIII, X = OH).—A solution of sodium nitrite (1 g. in 10 c.c.) was slowly added to a cold solution of 3-keto-2-*p*-aminophenyl-2:3-dihydrothionaphthen 1:1-dioxide (4 g.) in concentrated hydrochloric acid (10 c.c.). The crystalline material which separated was washed with aqueous sodium acetate, with water, and with ether. It formed deep red plates, which decomposed at  $123^{\circ}$  (Found: C, 58.1; H, 3.3;  $H_2O$ , 6.1.  $C_{14}H_8O_4S \cdot H_2O$  requires C, 57.9; H, 3.4;  $H_2O$ , 6.2%). The substance dissolved in warm concentrated hydrochloric acid, and when chloroplatinic acid was added to the solution the *chloroplatinate* was precipitated in the crystalline state [Found: Pt, 19.9.  $(C_{14}H_8O_4S \cdot HCl)_2PtCl_4$  requires Pt, 20.4%]. The *ferrichloride* was obtained in orange crystals by a similar method (Found: Fe, 12.6.  $C_{14}H_8O_4S \cdot HCl \cdot FeCl_3$  requires Fe, 11.9%). Both salts were unstable in presence of moisture and decomposed when heated. When a solution of the chloride was diluted, the hydroxide was produced.

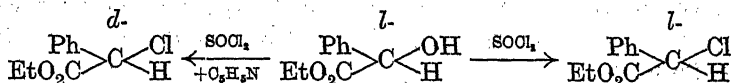
LVII.—*The Interaction of Ethyl l-Mandelate and Thionyl Chloride in the Presence of Pyridine. The Mechanism of the Replacement of Hydroxyl by Chlorine by Means of Thionyl Chloride.*

By JOSEPH KENYON, ALFRED GEORGE LIPSCOMB, and  
HENRY PHILLIPS.

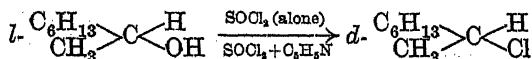
WHEN a laevorotatory hydroxy-acid or its ester is treated with thionyl chloride, the chloro-acid or ester produced is dextrorotatory; e.g., ethyl *l*-malate is converted into ethyl *d*-chlorosuccinate (McKenzie and Barrow, J., 1911, 99, 1910):



McKenzie and Clough (J., 1910, 97, 2564) discovered, however, that thionyl chloride behaves differently towards hydroxy-acids (and esters) containing a phenyl group directly attached to the asymmetric carbon atom, since from these compounds it produces chloro-acids (and esters) with the same sign of rotation as the parent hydroxy-compound; e.g., ethyl *l*-mandelate is converted into ethyl *l*-phenylchloroacetate (McKenzie and Barrow, *loc. cit.*). It has now been found that if ethyl *l*-mandelate is first dissolved in a tertiary base (pyridine, quinoline, or *isoquinoline*) and then treated with thionyl chloride, ethyl *d*-phenylchloroacetate is obtained instead of ethyl *l*-phenylchloroacetate. The following changes have therefore been realised:



These results are the more surprising since *l*-β-octanol is converted into *d*-β-chloro-octane by thionyl chloride both in the absence (Levene and Mikeska, *J. Biol. Chem.*, 1924, 59, 45) and in the presence of pyridine (McKenzie and Tudhope, *ibid.*, 1924, 62, 551):



There can be little doubt that the mechanism of the interaction of thionyl chloride with hydroxy-compounds is modified by the presence of a tertiary base. The work now described suggests, however, that such modification only determines the sign of rotation of the resulting chloro-compound when a phenyl group is directly attached to the asymmetric carbon atom.

In the paragraphs below, the results of the experiments are briefly described and then the mechanisms of the chlorination

reaction of thionyl chloride in the presence and in the absence of pyridine are discussed. An explanation is also put forward to account for the difference in behaviour of hydroxy-compounds which contain an aromatic radical.

*Results of the Experiments.*—Thionyl chloride (1 or 2 mols.) was added slowly to an ice-cold solution of ethyl *l*-mandelate and the tertiary base (1 or 2 mols.) in about five volumes of dry ether. After the initial vigorous reaction had ceased, the reaction mixture was warmed on a steam-bath for 30 minutes. Water was then added, and the product extracted with ether. The ethereal extract was washed with dilute hydrochloric acid and dried, and the product isolated and distilled. The ethyl *d*-phenylchloroacetate obtained was sometimes contaminated with ethyl *l*-mandelate, particularly in those experiments in which the *l*-ester was dissolved in only one molecular proportion of the tertiary base. This was most probably due to incomplete reaction under the mild experimental conditions employed, which were chosen to minimise the interaction between the chloro-ester produced and the tertiary base.

In Table I are recorded the rotatory powers of the ethyl *d*-phenylchloroacetate and of the mixtures of ethyl *d*-phenylchloroacetate and ethyl *l*-mandelate which were isolated. The percentages of *d*-chloro-ester in the mixtures were calculated from the percentages of chlorine which they were found to contain. For purposes of comparison, the rotatory power of the ethyl *l*-phenylchloroacetate prepared by McKenzie and Barrow (*loc. cit.*) is also included in the Table. The observed rotatory power of this *l*-ester ( $[\alpha]_{5461}^l$ ,  $l = 1.0$ ) was calculated from the recorded value ( $[\alpha]_{5893}^l$ ,  $l = 1.0$ ) by aid of the dispersion ratio  $\alpha_{5893}/\alpha_{5461}$  0.816, which was determined for this purpose.

TABLE I.

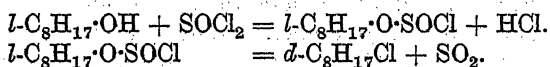
*The Observed Rotatory Powers of Ethyl Phenylchloroacetate prepared from Ethyl l-Mandelate by Means of Thionyl Chloride in the Presence of Tertiary Bases.*

Tertiary base used.	Observed rotatory power, $[\alpha]_{5461}^l$ ( $l = 1.0$ ).	% Ethyl phenylchloro- acetate in the product.	% Cl in the product.*
None (McKenzie and Barrow) .....	— 91.3°	100.0	—
Pyridine.			
1 mol.; SOCl <sub>2</sub> , 1 mol. ....	+ 41.2	63.3	11.3
2 mols.; SOCl <sub>2</sub> , 2 mols. ....	+ 122.0	100.0	18.0
Quinoline.			
1 mol.; SOCl <sub>2</sub> , 1 mol. ....	+ 107.2	83.3	14.9
2 mols.; SOCl <sub>2</sub> , 2 mols. ....	+ 116.2	100.0	17.7
isoQuinoline.			
1 mol.; SOCl <sub>2</sub> , 1 mol. ....	+ 114.4	100.0	18.2
2 mols.; SOCl <sub>2</sub> , 2 mols. ....	+ 73.0	88.4	15.8

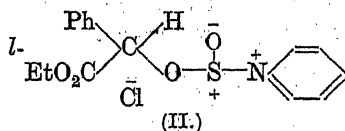
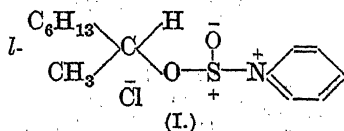
\* Ethyl phenylchloroacetate contains 17.9% Cl.

It will be seen that the magnitudes of the rotatory powers of the ethyl *d*-phenylchloroacetate obtained in these experiments were higher than that of the *l*-ester obtained by means of thionyl chloride alone. They are also greater than the rotatory power of the *d*-ester obtained by Walden (*Ber.*, 1895, **28**, 1287) by the action of phosphorus pentachloride on a solution of ethyl *l*-mandelate in chloroform. The rotatory power of this ester was  $[\alpha]_{5893} + 25.19^\circ$ , from which it can be calculated that it had  $\alpha_{5461} + 37.0^\circ$  ( $l = 1.0$ ).

*The Interaction of Thionyl Chloride with 1-β-Octanol and Ethyl l-Mandelate in the Presence of Pyridine.*—The reaction between thionyl chloride and an alcohol takes place in two stages. The alcohol is first converted into a chlorosulphinic ester, and this ester then loses sulphur dioxide and forms the chloride. In the case of *d*-amyl alcohol, McKenzie and Clough (*J.*, 1913, **103**, 698) were able to isolate the *d*-amyl chlorosulphinate and showed that by heating to  $120^\circ$  it was converted into *d*-amyl chloride. Similarly, Frankland and Garner (*J.*, 1914, **105**, 1101) have isolated ethyl *d*-α-chlorosulphinoxypionate. Attempts made in these laboratories to isolate *l*-β-octyl chlorosulphinate from the product of the interaction of *l*-β-octanol and thionyl chloride have been unsuccessful, the sole product obtained in every experiment being *d*-β-chloro-octane. Nevertheless, it is probable that this reaction, as with *d*-amyl alcohol, also occurs in two stages, and that the chlorosulphinic ester, which is the product of the first stage of the reaction, is difficult to isolate owing to its instability.

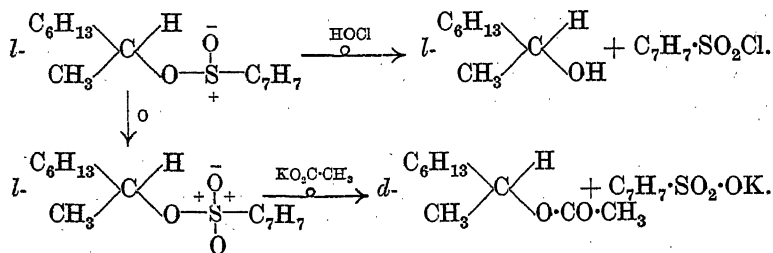


If pyridine were present, it could take part in both stages of the reaction. It could facilitate the formation of the chlorosulphinate, and also aid its decomposition by combining with it to form the unstable intermediate complex (I), a pyridinium chloride.

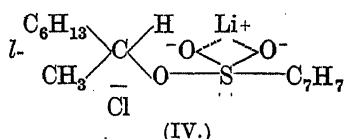
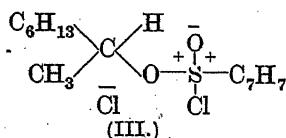


A similar unstable pyridinium chloride (II) might also arise during the reaction between ethyl *l*-mandelate and thionyl chloride in the presence of pyridine. The constitutions assigned to (I) and (II) involve few, if any, assumptions. It is also considered that they emphasise certain important characteristics of the unstable intermediate complexes the formation of which can be postulated in many reactions which lead to a Walden inversion. In previous

papers two reactions have been described which are known, with some degree of certainty, to take place with a Walden inversion. One is the conversion of *p*-toluenesulphonic esters into carboxylic esters (Phillips, J., 1923, **123**, 44; 1925, **127**, 2566; Kenyon, Phillips, and Turley, *ibid.*, p. 399; Gough, Hunter, and Kenyon, J., 1926, 2052), and the other the conversion of *l*- $\beta$ -octyl *p*-toluenesulphinate into *d*- $\beta$ -octanol (Houssa, Kenyon, and Phillips, J., 1929, 1700). The results obtained with the *p*-toluenesulphinate and the *p*-toluenesulphonate of *l*- $\beta$ -octanol were as follows:

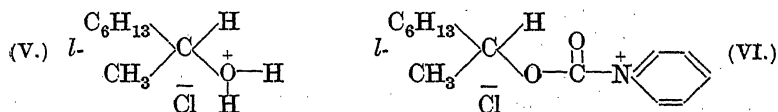


It was also found (Houssa, Kenyon, and Phillips, *loc. cit.*) that *d*- $\beta$ -chloro-octane could be obtained either by the action of chlorine on the *l*-sulphinic ester or by the action of lithium chloride on the *l*-sulphonic ester. It was considered highly probable that these reactions were also accompanied by an inversion, since they were similar to the corresponding reactions with hypochlorous acid and potassium acetate. On this assumption, *d*- $\beta$ -chloro-octane has the same configuration as *d*- $\beta$ -octanol. Houssa, Kenyon, and Phillips (*loc. cit.*), abandoning the  $\alpha$ -hydrogen hypothesis of Phillips (*loc. cit.*), made use of the revised structural formulæ for *p*-toluenesulphinic esters (Phillips, *loc. cit.*, p. 2552) and sulphonic esters (Sugden, Reed, and Wilkins, J., 1925, **127**, 1525), and suggested that during the reactions, mentioned above, which lead to the formation of *d*- $\beta$ -chloro-octane, the intermediate complexes (III) and (IV) were formed.



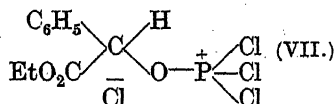
On comparing the constitutions assigned to these two complexes, the decomposition of which is accompanied by a Walden inversion, with those assigned to the complexes (I) and (II), certain striking similarities are found. In all four the group about to sever its union with the asymmetric carbon atom has become preponderantly

positive in character. Further, the chlorine atom, about to unite with the asymmetric carbon atom, exists in each case as a negative ion. It is also noteworthy that intermediate complexes possessing these two characteristics may also be formed during two other reactions, by the aid of which, and according to the conclusions of Houssa, Kenyon, and Phillips (*loc. cit.*), *l*- $\beta$ -octanol can be converted into *d*- $\beta$ -chloro-octane. These are the interaction of *l*- $\beta$ -octanol and hydrogen chloride (V) (Pickard and Kenyon, J., 1911, 99, 45) and the interaction of *l*- $\beta$ -octyl chlorocarbonate and pyridine (Houssa and Phillips, J., 1929, 2510) (VI).



By the interaction of *l*- $\beta$ -octanol and thionyl chloride, in the presence of pyridine (I), *d*- $\beta$ -chloro-octane is produced and therefore this reaction can also be assumed to take place with inversion of configuration. It thus appears that in all the reactions by which *l*- $\beta$ -octanol, *l*- $\beta$ -octyl *p*-toluenesulphonate or *p*-toluenesulphinate can be converted into  $\beta$ -chloro-octane a Walden inversion occurs. Moreover, each of these reactions and also those by which *l*- $\beta$ -octyl *p*-toluenesulphonate is converted into carboxylic esters of *d*- $\beta$ -octanol, and *l*- $\beta$ -octyl *p*-toluenesulphinate into *d*- $\beta$ -octanol, all pass through a phase in which unstable intermediate complexes, possessing certain notable characteristics in common, are produced.

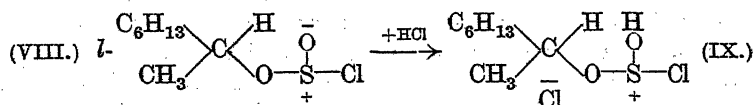
It will be assumed that since, during the reaction between ethyl *l*-mandelate and thionyl chloride in the presence of pyridine, the formation of an intermediate complex of the same type may also be postulated, this reaction is accompanied by a Walden inversion: in other words, that ethyl *l*-phenylchloroacetate has the same configuration as ethyl *l*-mandelate. It follows, therefore, on this assumption, that the interaction of ethyl *l*-mandelate and phosphorus pentachloride is also attended by a configurative change. It is significant that here again the same type of intermediate complex (VII) may arise.



A general idea underlying most of the theories of the Walden inversion (Fischer, *Annalen*, 1911, 381, 132; Werner, *Ber.*, 1911, 44, 881; Pfeiffer, *Annalen*, 1911, 383, 123; Gadamer, *Chem. Ztg.*, 1912, 36, 1327; Lowry, *Deuxième Conseil de Chimie. Solvay*, 1925, 40) is that in such reactions the entering group attaches itself to

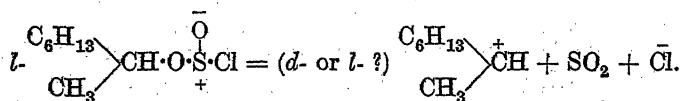
the opposite side of the asymmetric molecule to that occupied by the group to be displaced. It is essential, therefore, for the occurrence of a Walden inversion that the entering group should be free to take up this position. In the unstable intermediate complexes of the inversion reactions described in this paper, the entering group, the chlorine anion, is always available to assume this favourable position in the molecular complex, before the groups to be displaced leave the asymmetric carbon atoms.

*The Interaction of Thionyl Chloride with l-β-Octanol and Ethyl l-Mandelate in the Absence of Pyridine.*—With l-β-octanol. Levene and Mikeska (*loc. cit.*) have shown that the action of thionyl chloride on l-β-octanol in the absence of pyridine leads to the formation of d-β-chloro-octane; hence a Walden inversion occurs, since it has been concluded that d-β-chloro-octane has the same configuration as d-β-octanol. Furthermore, since the inversion is unlikely to occur during the first stage of the reaction (as the bonds of the asymmetric carbon atom are not disturbed), it follows that it takes place when the l-β-octyl chlorosulphinate decomposes.



It has been found that the interaction of thionyl chloride and l-β-octanol in the presence of potassium carbonate also leads to the formation of d-β-chloro-octane. This result indicates that the d-β-chloro-octane obtained in the absence of potassium carbonate does not arise from the interaction, as shown in (IX), of the chlorosulphinate with the hydrogen chloride produced in the first stage of the reaction.

It seems reasonable to assume that when the various intermediate complexes, which have been postulated, decompose, the asymmetric carbon atoms necessarily acquire a positive charge, since, ultimately, they each unite with a negative chlorine ion. It is therefore possible that, when l-β-octyl chlorosulphinate decomposes, it splits up into a carbonium kation, sulphur dioxide, and a chlorine anion, and that the d-β-chloro-octane is formed by the union of the carbonium ion with the chlorine ion :



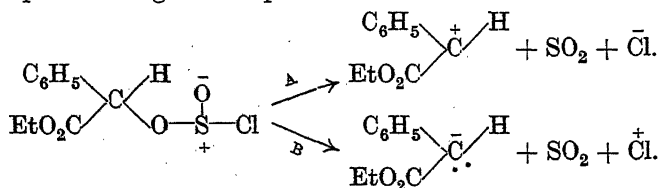
Experimental evidence, however, is still wanted which will show whether the formation of a carbonium kation is attended with a





a negative ion and a positively charged group (the nitrogen molecule) about to leave the asymmetric carbon atom.

*With ethyl l-mandelate.* McKenzie and Barrow (*loc. cit.*) have shown that thionyl chloride, in the absence of pyridine, converts ethyl *l*-mandelate into ethyl *l*-phenylchloroacetate. It has been suggested that these two compounds have the same configuration and therefore that the reaction is not accompanied by a Walden inversion. As in the study of the interaction of *l*- $\beta$ -octanol and thionyl chloride, an experiment was made to prove that the ethyl *l*-phenylchloroacetate was not formed by the interaction of the products of the first stage of the reaction, namely, hydrogen chloride and ethyl *l*-mandelylchlorosulphinate. It was found that potassium carbonate (*in marked contrast to pyridine*) had no influence on the sign of rotation of the ethyl phenylchloroacetate obtained. There appear to be two possible mechanisms (A and B) by which the decomposition might take place.



Of these two alternatives, only (B) sharply differentiates the decomposition of ethyl *l*-mandelylchlorosulphinate from that of *l*- $\beta$ -octyl chlorosulphinate and assigns a definite function to the phenyl group. This function is to confer on the asymmetric carbon atom the power to retain electrons during the decomposition. A phenyl group can function in this way, since it is strongly electron-attracting, whereas purely aliphatic groups, such as methyl and *n*-hexyl, are electron-donating groups, which, therefore, when attached to an asymmetric carbon atom, weaken its power to retain electrons. This mechanism also gives a satisfactory explanation of the power of pyridine to change the sign of rotation of the product of this decomposition. The interaction of pyridine with the chlorosulphinate produces a pyridinium chloride (II) in which the positive character of the chlorosulphinoxy-group has been augmented and its electron-retaining power therefore increased. Hence, when the chlorosulphinate decomposes in the presence of pyridine, the increased electron-retaining power of the chlorosulphinoxy-group enables it to overcome the electron-retaining power conferred on the asymmetric atom by the phenyl group, with the result that the asymmetric carbon atom loses two electrons during the further stages of the decomposition, which now leads to a Walden inversion.

## EXPERIMENTAL.

*l*-Mandelic acid, isolated from amygdalin (Freudenberg and Markert, *Ber.*, 1925, 58, 1753), was converted into ethyl *l*-mandelate by the method of Fischer and Speier.

*The Interaction of Thionyl Chloride with Ethyl l-Mandelate and d-β-Octanol in the Presence of Potassium Carbonate.*—With ethyl *l*-mandelate. Thionyl chloride (2.97 g.) in ether (10 c.c.) was added to a solution of ethyl *l*-mandelate (4.5 g.) in ether (50 c.c.) containing recently ignited potassium carbonate (10.4 g.). The mixture was heated under reflux for  $\frac{1}{2}$  hour, the potassium carbonate and chloride were removed by filtration, and the ether was distilled from the filtrate. The residue on distillation gave a mixture of ethyl *l*-mandelate and ethyl *l*-phenylchloroacetate, b. p. 136–138°/18 mm., with  $\alpha_{5461} -30.94^\circ$  ( $l = 0.25$ ) (Found: Cl, 7.7%). The mixture therefore contained 43% of the chloro-ester. 1.14 G. of ethyl *l*-mandelate were dissolved in 0.86 g. of ethyl *dl*-phenylchloroacetate. This solution had  $\alpha_{5461} -20.98^\circ$  ( $l = 0.25$ ) and hence the ethyl phenylchloroacetate in the mixture isolated in the above experiment was laevorotatory.

*With d-β-octanol.* *d*-β-Octanol (2.9 g.) in ether (30 c.c.) was added slowly to an agitated solution of thionyl chloride (10 g.) in ether (30 c.c.) containing potassium carbonate (12 g.). After 12 hours, the ether was removed by distillation, and the residue extracted with ether. In this manner the reaction was completed in the presence of potassium carbonate. The ethereal extract, on evaporation, gave *l*-β-chloro-octane (2.5 g.), b. p. 60–61°/14 mm. and  $\alpha_{5461} -5.05^\circ$  ( $l = 0.25$ ).

The authors wish to express their thanks to the Government Grant Committee of the Royal Society and to Imperial Chemical Industries, Ltd., for grants which have defrayed the cost of this investigation.

BATTERSEA POLYTECHNIC, S.W. 11.

[Received, December 5th, 1929.]

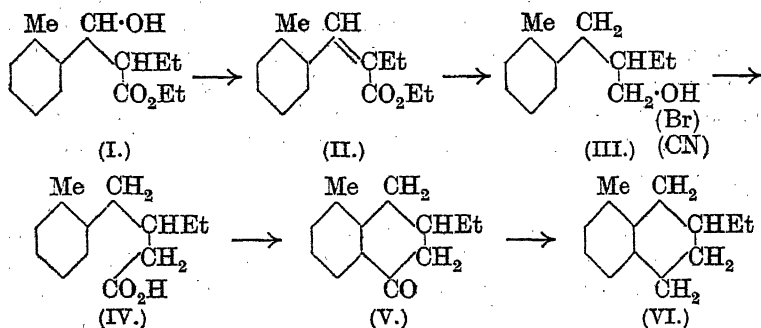
LVIII.—*Synthesis of Alkyl Naphthalenes. Part I.*  
5-, 6-, and 7-Ethyl-1-methylnaphthalenes.

By JOHN HARVEY, ISIDOR MORRIS HEILBRON, and  
DONALD GRAHAM WILKINSON.

IN connexion with the study now being carried out in this laboratory of the structure of the naphthalene hydrocarbon  $C_{13}H_{14}$  obtained by dehydrogenation of tetracyclosqualene with sulphur (Harvey, Heilbron, and Kamm, J., 1926, 3136) it became desirable to have,

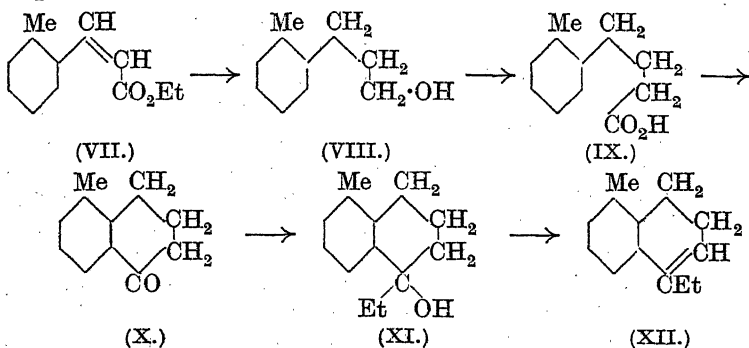
for reasons which will be explained in a later communication, information regarding the properties of the methylethynaphthalenes containing a methyl group in position 1 and the ethyl radical in the second benzene ring. The present communication deals with the synthesis of the three isomerides indicated above.

**1-Methyl-7-ethylnaphthalene.**—*o*-Tolualdehyde and ethyl  $\alpha$ -bromobutyrate were condensed together in presence of zinc, whereby ethyl  $\beta$ -hydroxy- $\beta$ -*o*-tolyl- $\alpha$ -ethylpropionate (I) was obtained. The hydroxy-ester was converted into ethyl *o*-methyl- $\alpha$ -ethylcinnamate (II) by treatment with phosphorus tribromide and subsequent removal of hydrogen bromide by heating with diethylaniline. Reduction of the unsaturated ester by Bouveault's method gave the alcohol (III), which was converted through the bromide and nitrile (compare Ruzicka, *Helv. Chim. Acta*, 1922, 5, 934) into  $\gamma$ -*o*-tolyl- $\beta$ -ethylbutyric acid (IV). Ring closure was brought about by the action of aluminium chloride on the acid chloride of (IV), an almost theoretical yield of the cyclic ketone (V) being obtained. The ketone was reduced by Clemmensen's method to 1-methyl-7-ethyl-5:6:7:8-tetrahydronaphthalene (VI), and this on treatment with selenium (compare Diels, Gädke, and Körding, *Annalen*, 1927, 459, 1) gave 1-methyl-7-ethylnaphthalene.

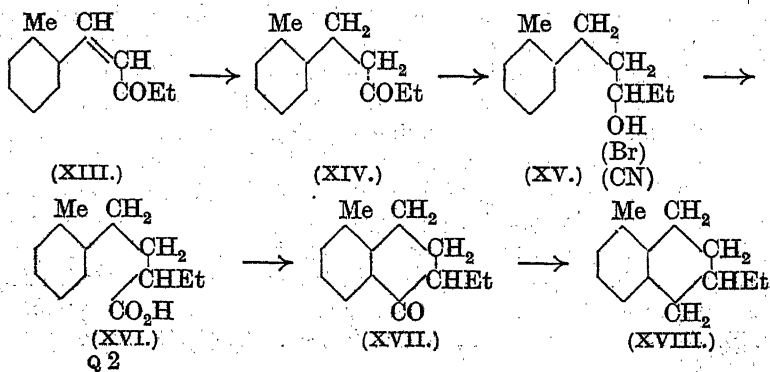


**1-Methyl-5-ethylnaphthalene.**—*o*-Tolualdehyde was condensed with ethyl acetate in presence of sodium, as described by Young (*Ber.*, 1892, 25, 2102), to ethyl *o*-methylcinnamate (VII), which was reduced with sodium and alcohol, in the apparatus described by Rupe and Länger (*Helv. Chim. Acta*, 1920, 3, 272), to  $\gamma$ -*o*-tolylpropyl alcohol (VIII). The alcohol was converted through the bromide and the nitrile into  $\gamma$ -*o*-tolylbutyric acid (IX), from which 5-keto-1-methyl-5:6:7:8-tetrahydronaphthalene (X) was obtained by the action of aluminium chloride on the acid chloride. The ketone on treatment with magnesium ethyl iodide yielded the hydroxy-compound (XI), which, on distillation or on heating with acetic anhydride, lost

water, giving 1-methyl-5-ethyl-7:8-dihydronaphthalene (XII). Dehydrogenation of this hydrocarbon by means of selenium gave the required 1-methyl-5-ethylnaphthalene.



1-Methyl-6-ethylnaphthalene.—2-Methylstyryl ethyl ketone (XIII), prepared by the condensation of *o*-tolualdehyde with methyl ethyl ketone in presence of alkali, on hydrogenation in presence of colloidal palladium, gave  $\beta$ -*o*-tolyl-diethyl ketone (XIV), and this on reduction with sodium gave a satisfactory yield of  $\gamma$ -*o*-tolyl- $\alpha$ -ethylpropyl alcohol (XV), from which  $\gamma$ -*o*-tolyl- $\alpha$ -ethylbutyric acid (XVI) was readily obtained in the usual manner. The acid was converted into its acid chloride, which on treatment with aluminium chloride gave an almost quantitative yield of 5-keto-1-methyl-6-ethyl-5:6:7:8-tetrahydronaphthalene (XVII). On reduction of the ketone by Clemmensen's method 1-methyl-6-ethyl-5:6:7:8-tetrahydronaphthalene (XVIII) was formed, and this was dehydrogenated with selenium, giving 1-methyl-6-ethylnaphthalene. A somewhat better yield of the alkylnaphthalene is obtained by reducing (XVII) with sodium and alcohol, whereby a mixture of carbinol and unsaturated hydrocarbon is produced which, without further purification, is treated with selenium.



## EXPERIMENTAL.

*Ethyl  $\beta$ -Hydroxy- $\beta$ -o-tolyl- $\alpha$ -ethylpropionate* (I).—A mixture of ethyl  $\alpha$ -bromobutyrate (72 g.) and freshly distilled *o*-tolualdehyde (45 g.) was added gradually to pure zinc turnings (26 g.) covered with dry benzene, in a flask fitted with a reflux condenser. After the addition of 20 c.c. of the mixture the flask was warmed on a steam-bath in order to start the reaction. The remainder was then added in small quantities at a time so as to regulate the reaction, and the whole refluxed for 4 hours. The product was decomposed with ice-cold dilute hydrochloric acid and the benzene layer was separated, washed with water, and dried over calcium chloride. After removal of the benzene the *hydroxy-ester* was fractionated in a vacuum and obtained as a thick oil (65 g.), b. p. 164–166°/12 mm. (Found: C, 70.8; H, 8.5.  $C_{14}H_{20}O_3$  requires C, 71.2; H, 8.5%).

*Ethyl o-Methyl- $\alpha$ -ethylcinnamate* (II).—A solution of the hydroxy-ester (65 g.) in dry benzene (100 c.c.) was heated on a water-bath with phosphorus tribromide (85 g.) until the evolution of hydrogen bromide had practically ceased (5 hours). The excess of phosphorus tribromide was decomposed with alcohol (with ice-cooling), the solution poured into water, and the benzene layer separated and dried over calcium chloride. After removal of the solvent, the bromo-ester was obtained as a heavy oil (82 g.) with an irritating effect on the eyes. Without further purification, it was mixed with diethylaniline (70 g.) and heated at 180° for 4 hours. Water was added, the whole extracted with ether, and the excess of diethylaniline removed by repeated washing with dilute hydrochloric acid. The residual unsaturated ester was fractionated under reduced pressure, practically the whole distilling at 144°/15 mm.

*$\gamma$ -o-Tolyl- $\beta$ -ethylpropyl Alcohol* (III).—A solution of the above ester (45 g.) in absolute alcohol (300 c.c.) was placed in a flask fitted with a sealed stirrer, a reflux condenser, and a short wide inlet tube. The stirrer was set in rapid motion and sodium (65 g.), cut into small strips, was added gradually through the inlet tube to the boiling solution. During the course of the reduction (1½ hours) more alcohol (200 c.c.) was added from time to time to assist the solution of the sodium. The liquid was diluted with water, the alcohol distilled, and the residual alkaline solution extracted with ether. The ethereal solution, after being washed with water, dried, and evaporated, gave 19–20 g. of the crude alcohol. When the aqueous solution was rendered acid,  *$\beta$ -o-tolyl- $\alpha$ -ethylpropionic acid* was precipitated as an oil. After being extracted in ether, it distilled as a thick oil, b. p. 173–175°/12 mm., which gradually solidified, and then separated from light petroleum in large colourless prisms, m. p. 53–54° (Found: C, 75.0; H, 8.5.  $C_{12}H_{16}O_2$  requires C,

75.0; H, 8.3%). The acid was esterified and reduced as described above; a further quantity of  $\gamma$ -o-tolyl- $\beta$ -ethylpropyl alcohol was then obtained. The whole was distilled, and the pure alcohol collected as a colourless viscous liquid, b. p. 145°/15 mm. (Found: C, 81.2; H, 10.2.  $C_{12}H_{18}O$  requires C, 80.9; H, 10.1%).

*$\gamma$ -o-Tolyl- $\beta$ -ethylpropyl Bromide.*—The alcohol (25 g.) was heated under pressure with a 30% solution of hydrogen bromide in glacial acetic acid (250 g.) at 100° for 16 hours. The cooled liquid was poured into water; the bromide then separated as a heavy oil, which was extracted with ether. The ethereal solution was washed and dried, and the residual bromide distilled, b. p. 136—138°/12 mm. Yield, quantitative (Found: Br, 32.7.  $C_{12}H_{17}Br$  requires Br, 33.2%).

*$\gamma$ -o-Tolyl- $\beta$ -ethylbutyric Acid (IV).*—A solution of the bromide (31 g.) in alcohol (500 c.c.) was boiled with potassium cyanide (25 g. in 70 c.c. of water) for 20 hours. The alcohol was then removed, and the residue diluted with water; the nitrile separated as an oil, which was directly hydrolysed by boiling for 40 hours with concentrated alcoholic potash (30 g. KOH). The crude acid was precipitated from the diluted alkaline solution, extracted with ether, and distilled,  *$\gamma$ -o-tolyl- $\beta$ -ethylbutyric acid* being obtained as a thick oil (21 g.), b. p. 186°/13 mm. (Found: C, 75.4; H, 8.8.  $C_{13}H_{18}O_2$  requires C, 75.7; H, 8.7%).

The acid chloride, prepared by treatment of the acid with thionyl chloride, was obtained as a colourless mobile oil, b. p. 149—150°/12 mm.

*5-Keto-1-methyl-7-ethyl-5:6:7:8-tetrahydronaphthalene.*—A solution of  $\gamma$ -o-tolyl- $\beta$ -ethylbutyryl chloride (19.5 g.) in petroleum (20 c.c., b. p. 80—100°) was gradually added to freshly prepared aluminium chloride (17 g.) covered with the same solvent. After the initial vigorous reaction had ceased, the mixture was heated on a steam-bath for 2 hours, and the product decomposed with ice-cold dilute hydrochloric acid. The ketone was extracted with ether and fractionated in a vacuum; a colourless oil, b. p. 165°/12 mm., was obtained which gradually solidified. On crystallisation from aqueous methyl alcohol, *5-keto-1-methyl-7-ethyl-5:6:7:8-tetrahydronaphthalene* (17 g.) separated in small needles, m. p. 38° (Found: C, 82.7; H, 8.7.  $C_{13}H_{16}O$  requires C, 83.0; H, 8.5%).

*1-Methyl-7-ethyl-5:6:7:8-tetrahydronaphthalene.*—The ketone (15 g.) was reduced by boiling with concentrated hydrochloric acid and amalgamated zinc (100 g.). When the greater part of the zinc had dissolved, the liquid was steam-distilled and the distillate extracted with ether. The crude tetrahydronaphthalene was fractionated, giving a mobile oil (6 g.), b. p. 129—131°/14 mm.

1-*Methyl-7-ethylnaphthalene*.—The tetrahydro-derivative was heated with powdered selenium (6 g.) at 300° for 24 hours. The reaction product was distilled over sodium, yielding a colourless oil (4.8 g.), b. p. 134–138°/14 mm., which was directly treated with warm alcoholic picric acid solution. The crude *picrate* which separated on cooling was recrystallised from alcohol, giving long, silky, golden-yellow needles (5 g.), m. p. 97° (Found : C, 56.7; H, 4.3; N, 10.7.  $C_{19}H_{17}O_7N_3$  requires C, 57.1; H, 4.3; N, 10.5%).

The *picrate* was decomposed with ammonia, and the hydrocarbon extracted with ether. 1-*Methyl-7-ethylnaphthalene* was obtained as a colourless oil, b. p. 133°/12 mm.,  $n_D^{20}$  1.5970, which failed to crystallise (Found : C, 91.4; H, 8.2.  $C_{13}H_{14}$  requires C, 91.8; H, 8.2%).

*Ethyl o-methylcinnamate* (VII) was prepared as detailed by Young (*loc. cit.*) from *o*-tolualdehyde and ethyl acetate in presence of sodium. The pure ester, which does not appear to have been described, was obtained as a highly refractive liquid, b. p. 157°/25 mm. (Found : C, 75.8; H, 7.6.  $C_{12}H_{14}O_2$  requires C, 75.8; H, 7.4%).

$\gamma$ -*o*-Tolylpropyl alcohol (VIII), obtained by reduction of the above ester (25 g.) as described under  $\gamma$ -*o*-tolyl- $\beta$ -ethylpropyl alcohol, formed a thick colourless oil (4 g.) with a sweetish odour, b. p. 136°/15 mm. The *urethane* formed long needles, m. p. 58°, from light petroleum (Found : N, 4.9.  $C_{17}H_{19}O_2N$  requires N, 5.2%).

$\beta$ -*o*-Tolylpropionic acid, which formed the main product (14 g.) in the Bouveault reduction, separated when the aqueous alkaline solution was rendered acid. It melted at 105°; Young (*loc. cit.*) gives m. p. 102° (Found : C, 73.1; H, 7.4. Calc. for  $C_{10}H_{12}O_2$  : C, 73.3; H, 7.3%). The acid was esterified, yielding 14 g. of the ethyl ester, b. p. 141°/22 mm., which was reduced to furnish a further quantity of the alcohol.

$\gamma$ -*o*-Tolylpropyl bromide formed a heavy, sweet-smelling liquid, b. p. 124°/17 mm. Yield, quantitative (Found : Br, 37.7.  $C_{10}H_{13}Br$  requires Br, 37.5%).

$\gamma$ -*o*-Tolylbutyric Acid (IX).—A solution of the bromide (25.5 g.) in alcohol (450 c.c.) was boiled with potassium cyanide (20 g. in 80 c.c. of water) for 24 hours. After removal of the alcohol the liquid was diluted with water and the nitrile then separated as an oil. It was extracted with ether and hydrolysed with alcoholic potash (26 hours), and the diluted solution acidified;  $\gamma$ -*o*-tolylbutyric acid was then precipitated as an oil which quickly solidified. On crystallisation from light petroleum it separated in needles (20 g.), m. p. 60° (Found : C, 74.3; H, 7.9.  $C_{11}H_{14}O_2$  requires C, 74.2; H, 7.9%). The acid chloride was obtained as a colourless mobile liquid, b. p. 143°/17 mm.



5-Keto-1-methyl-5:6:7:8-tetrahydronaphthalene (X) was prepared as described under (V). The reaction product was decomposed with ice-cold dilute hydrochloric acid, and the liquid steam-distilled. The distillate was extracted with ether; the ketone was then obtained as a crystalline solid. It separated from light petroleum in large crystals, m. p. 50—51° (yield, 5 g. from 7.5 g. of the acid chloride) (Found: C, 82.7; H, 7.7.  $C_{11}H_{12}O$  requires C, 82.5; H, 7.5%).

1-Methyl-5-ethyl-7:8-dihydronaphthalene (XII).—A solution of the ketone (6 g.) in dry ether (25 c.c.) was added gradually to a well-cooled solution of magnesium ethyl iodide, prepared from magnesium (3.3 g.), ethyl iodide (20 g.), and dry ether (100 c.c.). The reaction mixture was heated under reflux for 4 hours and then decomposed with ice-cold dilute hydrochloric acid. The ethereal layer was washed with water and dried over sodium sulphate. After removal of the solvent the viscous carbinol was directly converted into the hydrocarbon by boiling with acetic anhydride (30 c.c.) under reflux for 1 hour. The acetic anhydride was decomposed with hot water and the hydrocarbon was extracted with ether and purified by distillation over sodium under reduced pressure; it was then obtained as a colourless mobile liquid (4.5 g.), b. p. 130—131°/12 mm.

1-Methyl-5-ethylnaphthalene.—The dihydro-compound (8 g.) was heated with selenium (4.2 g.) at 300° for 24 hours. The solid reaction product was distilled over sodium; the main portion, b. p. 133°/10 mm., was directly converted into picrate by treatment with warm alcoholic picric acid solution. On cooling, the *picrate* crystallised in small orange needles (13 g.), m. p. 97° (Found: C, 56.8; H, 4.4; N, 10.5.  $C_{19}H_{17}O_7N_3$  requires C, 57.1; H, 4.4; N, 10.5%).

1-Methyl-5-ethylnaphthalene was regenerated by treating the picrate, suspended in ether, with dilute aqueous ammonia. It crystallised from alcohol in plates, m. p. 40°, closely resembling naphthalene in appearance and odour;  $n_D^{30}$  1.600.

2-Methylstyryl Ethyl Ketone (XIII).—A solution of *o*-tolualdehyde (46 g.) and methyl ethyl ketone (52 g.) in 50% alcohol (800 c.c.) was treated with 2*N*-sodium hydroxide solution (20 c.c.), and the whole left over-night; 2-methylstyryl ethyl ketone then separated as a heavy yellow oil. After dilution with water the liquid was extracted with ether, and the ethereal solution dried over sodium sulphate. The residual oil was distilled, the main fraction passing over at 145—160°/14 mm. After further fractionation the ketone was obtained as a pale yellow oil (19 g.), b. p. 150—153°/14 mm.

The *semicarbazone*, prepared in the usual manner, crystallised from acetone in colourless needles, m. p. 176—178°; it exhibited

phototropic properties, becoming bright yellow on exposure to sunlight (Found: N, 18.2.  $C_{13}H_{17}ON_3$  requires N, 18.2%).

*β-o-Tolyldiethyl Ketone* (XIV).—2-Methylstyryl ethyl ketone (18 g.) was dissolved in dry ether (200 c.c.) and hydrogenated at room temperature in presence of palladium-black. After the absorption of hydrogen had ceased, the ether was removed and the residual oil distilled, the *ketone* being obtained as a pale yellow liquid (17 g.), b. p. 140–143°/16 mm. (Found: C, 81.4; H, 8.9.  $C_{12}H_{16}O$  requires C, 81.8; H, 9.1%). The *semicarbazone* crystallised from alcohol in plates, m. p. 160° (Found: C, 66.6; H, 8.2; N, 18.2.  $C_{13}H_{19}ON_3$  requires C, 66.9; H, 8.2; N, 18.0%).

*γ-o-Tolyl-α-ethylpropyl Alcohol* (XV).—A solution of the above ketone (15.2 g.) in boiling absolute alcohol (150 c.c.) was reduced by means of sodium (20 g.), added in small quantities at a time. The reaction mixture was diluted with water and extracted with ether. After removal of the solvent the alcohol was distilled in a vacuum, forming a colourless viscous oil (12.5 g.), b. p. 145–146°/14 mm. (Found: C, 80.7; H, 10.2.  $C_{12}H_{18}O$  requires C, 80.9; H, 10.1%).

*γ-o-Tolyl-α-ethylpropyl bromide*, prepared as already described (p. 427), formed a colourless mobile liquid, b. p. 149–151°/18 mm. (Found: Br, 32.6.  $C_{12}H_{17}Br$  requires Br, 33.2%).

*γ-o-Tolyl-α-ethylbutyric Acid* (XVI).—A solution of the bromide (12.5 g.) in alcohol (200 c.c.) was boiled with potassium cyanide (15 g. in 40 c.c. of water) for 30 hours. The alcohol was removed, and after dilution with water, the residue was extracted with ether. The crude product was distilled under reduced pressure, and yielded together with the nitrile fraction, b. p. 150–165°/16 mm. (6 g.), a lower-boiling fraction consisting of unsaturated hydrocarbons (3 g.). The nitrile was hydrolysed with amyl-alcoholic potash (potassium hydroxide, 10 g., in 100 c.c. of amyl alcohol) for 15 hours, and the amyl alcohol removed with steam. When the solution was acidified, *γ-o-tolyl-α-ethylbutyric acid* was precipitated as an oil, which was extracted with ether and distilled. The acid was collected as a viscous oil, b. p. 195–196°/18 mm., which solidified after some days. It crystallised from light petroleum in large prisms (4.5 g.), m. p. 51° (Found: C, 75.6; H, 8.8.  $C_{13}H_{18}O_2$  requires C, 75.7; H, 8.7%). The acid chloride was obtained as a colourless liquid, b. p. 158–160°/18 mm.

*5-Keto-1-methyl-6-ethyl-5 : 6 : 7 : 8-tetrahydronaphthalene* (XVII) was prepared from the acid chloride (9 g.) as described on p. 427. The pure ketone (8 g.) was a colourless oil, b. p. 172°/19 mm. (Found: C, 82.9; H, 8.6.  $C_{17}H_{16}O$  requires C, 83.0; H, 8.5%).

*1-Methyl-6-ethylnaphthalene*.—A portion of the ketone (3.7 g.)

was reduced by Clemmensen's method, giving 2 g. of 1-methyl-6-ethyl-5 : 6 : 7 : 8-tetrahydronaphthalene, b. p. 130°/16 mm. The remainder of the ketone (4.5 g.) was dissolved in alcohol and heated with sodium (7 g.) at 130°. After removal of the alcohol the liquid was diluted with water and extracted with ether. The residual oil was distilled, the greater part (2.4 g.) passing over at 110—160°/20 mm. It was unsaturated towards bromine, and was probably a mixture of unsaturated hydrocarbon and carbinol. The products from both experiments were mixed together and heated with an equal weight of selenium at 300° for 24 hours. The oil was diluted with ether, filtered from unchanged selenium, and purified by distillation over sodium. The crude hydrocarbon (3.1 g.), b. p. 145—152°/20 mm., was converted into the *picrate*, which crystallised from alcohol in small yellow needles, m. p. 82° (Found : C, 56.8; H, 4.4; N, 10.4.  $C_{19}H_{17}O_7N_3$  requires C, 57.1; H, 4.3; N, 10.5%).

1-Methyl-6-ethylnaphthalene, which was regenerated from the pure picrate, formed a colourless, highly refractive liquid having a faint naphthalene-like odour; b. p. 140°/12 mm.,  $n_D^{20}$  1.598 (Found : C, 91.4; H, 8.3.  $C_{13}H_{14}$  requires C, 91.8; H, 8.2%).

Grateful acknowledgment is made to the Department of Scientific and Industrial Research for grants which have enabled this investigation to be carried out.

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# LIX.—*The Nature of the Alternating Effect in Carbon Chains. Part XXXII. The Directive Influence of $\psi$ -Basic Systems in Aromatic Substitution. Nitration of Benzylidene-m-nitroaniline.*

By JOHN WILLIAM BAKER and CHRISTOPHER KELK INGOLD.

THE study of orientation by neutral and by ionic substituents has a natural sequel in the consideration of directive action by the intermediate class of "ionogenic" groups, that is, neutral systems which tend to acquire an ionic charge by interaction with the reagent employed for further substitution. This category comprises not only simple acidic and basic substituents with a single potentially ionic centre (e.g., OH,  $NR_2$ ), but also  $\psi$ -acidic and  $\psi$ -basic groups, the ionic forms of which are regarded as possessing a distributed charge; and in Part XXXI (Baker, J., 1928, 2257) it was shown, by reference to the nitration of some  $\psi$ -acidic phenylnitromethanes, that the anionic charges, which are developed in the side chains of these

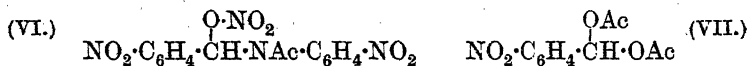


"Intensely yellow" is certainly a correct description; but the base itself is almost colourless and forms colourless solutions in dry alcohol. It is true that Flürscheim and Holmes prepared a "colourless" solid hydrochloride by precipitation with hydrogen chloride in dry benzene, but this might well be a non-ionised form, such as a  $\psi$ -salt,  $\text{Ph}\cdot\text{CHCl}\cdot\text{NHR}$ , which (like triphenylchloromethane and many other substances) might develop colour in suitable ionising solvents (see below); it does, indeed, form a strongly yellow solution in dry alcohol. Our experiments lead us to suggest that, on the contrary, the free base, for all practical purposes, is absent, and that the compound exists entirely as a sulphate in the sulphuric acid medium. This conclusion is based largely on partition experiments. When a solution of the base in ligroin is shaken with the acid, the whole of the base passes into the acid (with development of the usual strong colour). When a saturated solution of the base in the acid is shaken repeatedly with ligroin, or even with carbon tetrachloride, in which the base is very soluble, none is removed.\* Finally, when a warm concentrated solution of the base in the acid is cooled to the ordinary temperature and kept, the *hydrogen sulphate* separates. This salt, when dry, is almost colourless; but it gives the usual strong colour on solution in sulphuric acid.

Flürscheim and Holmes's second argument is that the high proportion of *m*-isomeride cannot be due to nitration of the ammonium kation, which "fact," according to them, is "established" by the observations that the *m*-ratio remained nearly the same when ammonium sulphate was added to the nitration solvent, whereas in the nitration of diethylbenzylamine (*idem*, J., 1926, 1569), admittedly a reaction of the kation, the addition of ammonium sulphate caused the *m*-ratio to be strongly depressed. Our observations compel us to challenge this conclusion also. It is true that, under the conditions used by Flürscheim and Holmes for the nitration of the Schiff's base, the addition of ammonium sulphate makes no great difference to the proportion of *m*-isomeride; but we find that precisely the same is true of the nitration of diethylbenzylamine. Furthermore, although careful observation shows that there is a small difference, which will be considered later, between the two cases, the direction of the disparity is the opposite of that suggested by Flürscheim and Holmes.

\* Neither is benzaldehyde extracted, which proves the absence of hydrolysis, since added benzaldehyde is readily removed. Indeed, if benzaldehyde and *m*-nitroaniline are brought together in the solvent, rapid combination occurs with formation of the anhydro-base, which, since it is present as sulphate, cannot be partitioned with neutral solvents, but can be recovered in good yield by pouring the acid solution into excess of ice-cold sodium hydrogen carbonate solution.

In seeking confirmatory evidence of the theory that nitration of the Schiff's base proceeds through the salt, we first studied its nitration with a nearly neutral reagent, namely, acetyl nitrate, the expectation being that salt formation would occur only to a small extent or not at all, and that, consequently, the proportion of *m*-isomeride would be found to be below the value, 79%, given by benzaldehyde in mixed acids. This was confirmed, the proportion found being 41%; but it soon transpired that the result could not justly be regarded as evidence on the question at issue, since at least one derivative of the Schiff's base other than its salt was almost certainly present in the nitration medium. From a solution of *m*-nitrobenzylidene-*m*-nitroaniline in this medium we have isolated an unstable crystalline compound which may have the constitution (VI), and it is possible, therefore, that nitration of benzylidene-*m*-nitroaniline takes place at least partly through a similar addition compound with acetyl nitrate. In this connexion the following analogy also seems to have some value: when benzaldehyde was nitrated with acetyl nitrate in excess of acetic anhydride, it was found possible to isolate the *p*-nitro-additive compound (VII); and the proportion of *m*-nitro-product in the mononitro-compounds was only 37%.



We therefore resumed the comparative study of the nitration of benzyldiethylamine and the Schiff's base in sulphuric acid with and without ammonium sulphate, on the basis of the following considerations. First, we concur with Flürscheim and Holmes in assuming that, *if* the Schiff's base is nitrated essentially as such, the depression in the *m*-ratio caused by sulphate ions should be negligible in comparison with that observed in a corresponding experiment with benzyldiethylamine, in which it is known that nitration occurs through the kation of the salt and that sulphate ions cause electrostriction equivalent to a certain amount of change in the direction, dissociated kation  $\longrightarrow$  undissociated salt; this difference, *if established*, would, we agree, constitute strong evidence that the azomethine is nitrated as base. Secondly, we suggest that if, on the other hand, the Schiff's base, like benzyldiethylamine, is nitrated through the kation of its salt, then, if there is any observable difference of behaviour, it should be the Schiff's base which should exhibit the larger repression of *m*-substitution when nitrated in the presence of sulphate ions. The reason is that the Schiff's base is a pseudo-base and that any association of the ions of the true (electrovalent) salt should be succeeded by partial conversion of this into

the pseudo-(covalent) salt; in other words, whilst any depression of the *m*-ratio in the nitration of benzyldiethylamine is dependent on the loss of *m*-orienting power represented by the change, ion  $\rightarrow$  salt, *i.e.*, pole  $\rightarrow$  dipole, in the case of the Schiff's base a further *m*-repressing influence exists in the second stage of the change, ion  $\rightarrow$  salt  $\rightarrow$   $\psi$ -salt, *i.e.*, pole  $\rightarrow$  dipole  $\rightarrow$  neutral form. A difference in this direction would therefore be strong evidence in favour of the theory that the nitration of the azomethine, leading to the high proportion of *m*-isomeride, takes place through the ion of the salt. The details of our nitrations are given in the experimental portion, but Table I constitutes a summary of the results relating to the point at issue. The figures represent the mean values of the percentage of *m*-isomeride, together with the mean deviations from the mean to give an indication of consistency.

TABLE I.

Diethylbenzylamine.		Benzylidene- <i>m</i> -nitroaniline.	
Conditions.	meta (%).	Conditions.	meta (%).
Without (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ...	61.0 $\pm$ 1.3	Without (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ...	89.1 $\pm$ 0.3
With (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ...	61.9 $\pm$ 0.3	With (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ...	83.7 $\pm$ 0.2
Diff. ...	+0.9 $\pm$ 1.6	Diff. ...	-5.4 $\pm$ 0.5

The difference here recorded for benzyldiethylamine is within the experimental error; no importance can be attached to it, and the only possible conclusion is that any alteration of the *m*-ratio caused by ammonium sulphate cannot be detected in the experiments we have conducted. On the other hand, the difference for benzylidene-*m*-nitroaniline, although not large, is well beyond the limits of precision, and affords clear evidence of nitration through the kation of the salt, confirming the indications of the experiments described earlier in this paper.

Thus it transpires that a reinvestigation of this crucial nitration reverses the theoretical situation in the direction favourable to those theories of aromatic substitution which are directly or indirectly related to the electronic theory of valency; and the same investigation shows that the theory of the distributed charge in  $\psi$ -basicity, as well as in  $\psi$ -acidity, is to be seriously regarded in its application to orientation by ionogenic systems.\*

#### EXPERIMENTAL.

*Materials.*—The benzylidene-*m*-nitroaniline employed had m. p. 72°, and was almost colourless (very pale greenish-yellow) (Found :

\* The application of this theory to the nitration of benzylidene-*m*-nitroaniline was made by the undersigned shortly after the appearance of Flürscheim and Holmes's publication, despite their claim to have proved the contrary (*Ann. Reports*, 1928, 25, 140).—C. K. I.

C, 68.8; H, 4.2. Calc.: C, 69.0; H, 4.4%). Following Flürscheim and Holmes's procedure, the sulphuric acid used for nitration contained a small excess of sulphur trioxide as a precaution against hydrolytic fission; for the same reason, the nitric acid employed was rendered anhydrous by distillation with excess of sulphuric acid.

*Salts of Benzylidene-m-nitroaniline.*—The base formed a colourless solution in alcohol dried with calcium, but a yellow solution in concentrated or fuming sulphuric acid. The hydrochloride, prepared by Flürscheim and Holmes's method, gave a yellow solution in calcium-dried alcohol and a yellow solution in concentrated or fuming sulphuric acid. The *hydrogen sulphate* was obtained as follows: The base (3.5 g.) was added in small portions with shaking to sulphuric acid (10 g.) containing 2.7% excess sulphur trioxide. The warm suspension was filtered through asbestos with precautions against access of moisture from the atmosphere, and the saturated solution of the sulphate kept in a sealed vessel at the ordinary temperature for several days, crystals slowly separating; these were collected and washed with ethyl sulphate and dry ether successively, or with ether only. A further quantity was precipitated from the mother-liquor by dilution with dry ether. The salt (Found:  $\text{SO}_4''$ , 32.4.  $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{SO}_4$  requires  $\text{SO}_4''$ , 29.6%) is very pale yellow, is comparatively stable in air, has m. p.  $225^\circ$  (decomp.) with previous darkening, and gives a yellow solution in fuming sulphuric acid.

*Partition Experiments.*—The ligroin (b. p.  $110$ – $120^\circ$ ) and carbon tetrachloride used were purified by repeated and prolonged shaking, first with concentrated and finally with fuming sulphuric acid (5% sulphur trioxide). The solvent for the second phase was sulphuric acid containing 2.7% excess of sulphur trioxide. The temperature was that of the room and the mixtures were shaken for periods varying from 1 to 24 hours. The results are summarised in the introduction.

*Formation of Azomethines in Sulphuric Acid.*—The acid used as solvent and condensing agent contained 2.7% excess of sulphur trioxide. The formation and isolation of benzylidene-*m*-nitroaniline have already been described; a similar experiment with *m*-nitrobenzaldehyde in place of benzaldehyde yielded *m*-nitrobenzylidene-*m*-nitrobenzylamine, which was similarly isolated. The product in each case was identified by m. p. and mixed m. p. with authentic specimens.

*Side-chain Transformations of an Azomethine and of Benzaldehyde with Nitric Acetic Anhydride.*—(Nitration 3). Benzylidene-*m*-nitroaniline (2.3 g.) was added in small portions at  $35^\circ$  to a mixture



prepared at 0° of absolute nitric acid (6.0 g.) and acetic anhydride, and the mixture was kept at room temperature over-night. The product was poured on ice and excess of potassium hydrogen carbonate and extracted with ether and benzene after decomposition of the acetic anhydride. Qualitative separation of the residue showed that substances other than nitrobenzylidene-*m*-nitroanilines were present, but the mixture was too complex to admit of the isolation of a pure individual. The whole process was therefore repeated with *m*-nitrobenzylidene-*m*-nitrobenzylamine in place of the original azomethine, except that the separation by means of ether and alkali was replaced by evaporation to constant weight at the ordinary temperature in an oil-pump vacuum with passage of a limited stream of dry air. The gain in weight was 42.4%, whereas the gain required for the addition of 1 mol. of acetyl nitrate is 38.8%. The material was not crystalline, but a product which remained crystalline for a short time was obtained as follows. A moderately concentrated solution of *m*-nitrobenzylidene-*m*-nitroaniline in a similarly prepared mixture of nitric acid and acetic anhydride was cooled in liquid ammonia for several hours; the liquid then became filled with a mass of colourless crystals. These rapidly dissolved if the temperature was raised, and were therefore collected at -30° in jacketed apparatus and washed with ethyl nitrate and ligroin at the same temperature. The crystals had m. p. 50—55° (decomp.) when rapidly heated in a sealed tube, but quickly decomposed at the ordinary temperature, either in the air or in sealed tubes, giving nitrous gases and a red gum. The freshly prepared crystals when warmed with dilute sulphuric acid gave nitric acid (nitron precipitate) in addition to the normal hydrolysis products. These experiments are regarded as proving the formation, rather than the constitution, of an addition product of the azomethine with the reagent used.

(Nitration 5). Benzaldehyde (5.0 g.) was added during 2 hours at 35° to a nitration solution prepared at 0° from absolute nitric acid (18 g.) and acetic anhydride (30 c.c.). After being kept over-night, the mixture was poured on ice and excess of potassium hydrogen carbonate, and, after decomposition of the acetic anhydride, extracted twice with ether and once with benzene. The residue obtained after removal of the solvents partly crystallised, and the crystals were drained and washed with ether-ligroin. They then had m. p. 118—120°, and one crystallisation from ether raised this to 125—127°, alone or in admixture with an authentic specimen of *p*-nitrobenzylidene diacetate.

*Nitration of Benzylidene-m-nitrobenzylamine and of Benzaldehyde in Acetic Anhydride.*—The numerical particulars, except analyses,

relating to these nitrations are given in Table II; the analytical details and results are in Table IV.

The products of the nitration of the azomethine were isolated as described for nitration 3 above, and hydrolysed by boiling with dilute sulphuric acid. The aldehydes were isolated by extraction with ether and benzene successively, and oxidised with permanganate to acids, which were isolated and analysed by reduction and bromination as usual.

The nitration product of benzaldehyde was isolated in the same way, and the subsequent treatment was the same except for the omission of the hydrolysis.

TABLE II.

Nitr- ation No.	Substance nitrated.	Weight taken (g.).	HNO <sub>3</sub> (g.).	Ac <sub>2</sub> O (g.)	Temp.	Time (hrs.).	Pro- duct (g.).	Treated (g.).	Acids (g.).
1	PhCH:NR	2.00	6.08	25	{ 0° room	{ 2.2 0.8 }	2.68	2.18	0.916
2	"	2.29	7.0	11.5	{ 35° room	{ 2.5 24.0 }	2.640	2.037	1.002
4	PhCH:O	4.98	18.0	30	{ 35° room	{ 2.0 20.0 }	10.40	4.682	2.480

The heading "Treated" should be interpreted, "Product hydrolysed and oxidised" for nitrations 1 and 2, and "Product oxidised" for nitration 4.

In nitration 1 the azomethine was previously dissolved in half the acetic anhydride, and the solution was slowly added to a mixture of the nitric acid and the other half.

In nitration 2 the solid azomethine was added in small portions to the nitration mixture.

In nitration 4 the benzaldehyde was run into the nitration solution. Part of the solution of the acids obtained by oxidation was lost and the weight recorded is that of the residue from the remaining solution.

*Nitration of Benzyl-diethylamine and Benzylidene-m-nitroaniline in Sulphuric Acid with and without Addition of Ammonium Sulphate.*—The numerical particulars, except analyses, relating to these nitrations are recorded in Table III; the analytical details and results will be found in Table IV.

The benzyl-diethylamine, b. p. 105–107°/20 mm., was in all cases run into the nitration solution. The product was poured on ice, basified with potassium hydroxide, and extracted with chloroform. Owing to the difficulty of removing the last traces of this solvent from the residual oil, some of the recorded yields of nitro-bases may be slightly too high. The products were oxidised, and the acids analysed, as usual.

The solid benzylidene-*m*-nitroaniline was in all cases added little

by little without solvent to the nitration solution. The product was poured on ice and excess of potassium hydrogen carbonate and extracted successively with ether and benzene. The material obtained was subjected to the usual routine of hydrolysis, oxidation, reduction, and bromination.

TABLE III.

Nitr ation No.	Sub- stance nitrated.	Weight taken (g.).	Am. SO <sub>4</sub> (g.).	HNO <sub>3</sub> (g.).	H <sub>2</sub> SO <sub>4</sub> (g.).	SO <sub>3</sub> % in H <sub>2</sub> SO <sub>4</sub> .	Temp.	Time (hrs.).	Pro- duct (g.).	Alde- hydes (g.).	Treated (g.).	Acids (g.).
6	PhCH <sub>2</sub> -NEt <sub>2</sub>	3.00	—	3.06	66	1.5	0° room	2.0 2.0	2.817	—	2.268	1.321
7	"	2.66	—	1.50	38	2.7	0° room	1.5 2.0	3.253	—	2.005	1.173
8	"	3.01	—	1.60	20	5.0	0° room	2.0 2.0	3.795	—	3.131	0.908
9	"	3.00	35	3.06	66	1.5	0° room	2.0 2.0	3.581	—	2.654	1.209
10	"	3.98	26	2.00	57	2.7	0° room	1.5 2.0	4.751	—	3.379	2.380
11	"	3.08	6	1.8	20	5.0	0° room	2.0 2.0	3.795	—	2.843	1.414
12	PhCH <sub>2</sub> NR	3.00	—	2.45	71	1.5	35-40° room	4.0 22.0	—	1.824	1.824	1.321
13	"	3.00	—	0.60	16.5	2.7	10° room	1.0 21.0	3.410	—	2.254	1.198
14	"	3.00	21	2.40	40	2.7	40° room	3.0 21.0	—	1.968	1.968	1.062
15	"	3.00	21	2.40	40	2.7	35-40° room	4.0 20.0	—	1.601	1.601	1.264

The heading "Treated" should be interpreted "Product oxidised" for nitrations 6—11, "Product hydrolysed and oxidised" for nitration 13, and "Aldehydes oxidised" for nitrations 12, 14, and 15. The corresponding figures for nitrations 6—11 may be somewhat too high owing to the difficulty, mentioned above, of completely freeing the oily nitration product from chloroform.

In nitration 8, part of the solution of the acids obtained by oxidation was lost and the weight recorded is that of the residue from the remainder.

In nitration 13, the 2.254 g. of nitration product yielded 1.645 g. of aldehydes and the whole of this was oxidised.

In nitrations 12, 14, and 15, the nitration products were hydrolysed without weighing, but the aldehydic product was weighed and the whole of it oxidised.

*Analytical Results relating to the Nitrations.*—The analytical data and the proportions of isomeride calculated therefrom are given in Table IV.

Table I (p. 435) shows the mean values (and mean deviations) of the proportion of *m*-nitro-isomeride formed from benzyldiethylamine and from benzylidene-*m*-nitroaniline in mixed acids, together with difference figures indicating the effect of ammonium sulphate on the meta-ratio; in the latter case, the mean deviations are obtained by subtracting one from another the individual results taken in pairs.

It should be stated that the experimental conditions (temperature,

proportions of reagents, etc.) relating to the individual nitrations of which the results are averaged are not exactly the same (Table III); nevertheless, the internal consistency of the results of each of the several sets so treated is such as to show that any differences due to the varied conditions referred to are too small to be detected by the experiments here recorded.

TABLE IV.

Recovered (g.).					Composition.					Percentage	
Nitr- ation No.	Acids analysed (g.).	$C_6H_5\cdot CO_2H$	$C_6H_5Br\cdot NH_2$	$C_6H_5Br\cdot CO_2H$	Acids.			nitro-isomerides.			
					$R\cdot CO_2H$ (mols. %).						
					$R =$ $C_6H_5\cdot$	$op\cdot$ $NO_2\cdot C_6H_4\cdot$	$m\cdot$ $NO_2\cdot C_6H_4\cdot$	$op\cdot$	$m\cdot$		
1	0.725	0.550	0.041	0.046	95.0	2.5	2.5	(50ca.)	(50ca.)		
2	0.862	0.015	0.815	0.624	2.8	57.6	39.6	59.3	40.7		
4	0.9115	0.015	1.047	0.773	2.3	59.1	38.6	62.6	37.4		
6	0.805	0.012	0.600	0.998	2.1	39.7	58.2	40.4	59.6		
7	0.835	0.014	0.601	1.030	2.4	38.8	58.8	39.6	60.4		
8	0.734	0.048	0.483	0.928	9.0	33.7	57.3	37.0	63.0		
9	0.777	0.025	0.550	0.984	4.6	37.0	58.4	38.7	61.3		
10	1.008	0.066	0.662	1.223	9.1	34.5	56.4	38.0	62.0		
11	0.720	0.009	0.497	0.930	1.8	37.2	61.0	37.7	62.3		
12	0.903	0.014	0.175	1.573	3.2	10.8	86.0	11.2	88.8		
13	0.681	0.209	0.090	0.845	40.4	6.5	53.1	10.7	89.3		
14	0.790	0.260	0.136	0.799	45.5	8.8	45.7	16.1	83.9		
15	0.857	0.473	0.063	0.360	77.2	3.8	19.0	16.5	83.5		

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### LX.—Primary and Associated Results of Replacement of Hydrogen directly attached to 4-Co-ordinated Carbon.

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THE substituents  $NO_2$ ,  $CN$ ,  $COR$ , and  $SO_2R$  in attachment to phenyl are meta-directive. In position X, in  $X\cdot CHR_1R_2$ , these substituents render the hydrogen atom labile and, moreover, the compound  $X\cdot CHR_1R_2$  is able to exist in two "tautomeric" forms. These relations were recognised nearly thirty years ago (compare J., 1901, 79, 1901).

It is not easy to state when the idea was first advanced that enolisation of a ketonic form originates in a minute degree of ionisation of the hydrogen atom which is attached to the carbon atom in the  $\alpha$ -position. It was certainly no later than 1902, when definite schemes based on this idea were proposed for reversible desmotropic changes belonging to the type now commonly called prototropic (J., 1902, 81, 1508). References were given in this

paper to still earlier suggestions, in which conceptions of dissociation had been applied to such phenomena by Brühl, Thiele, and Henrich, and the names of Kekulé, Williamson, Euler, Goldschmidt, Knorr, and others should have been mentioned in any exhaustive treatment.

The conception of the acceleratory influence of an alkali on enolisation as due to the attack of hydroxyl ion on an "incipiently ionised" hydrogen atom in direct attachment to carbon on the ketonic form was formulated in 1920 (*Mem. Manchester Phil. Soc.*, 1921, 64, 13 and 14).

The above ideas are now widely used, but few of those who have adopted them as working hypotheses appear to be aware that even the most recent of them took definite shape nearly nine years ago.

On the view above described, expressed in terms of current theory, compounds of the type  $X\cdot CHR_1R_2$  ( $X$  being defined as above) are themselves very feeble acids—too feeble, as a rule, to yield their protons to the very weak base, water, but able to yield them to more potent acceptors.

With the introduction of electronic conceptions it followed naturally, as Lewis himself pointed out, that the affinity of an acid must be associated with the degree of restraint on the bonding electrons of the atom to which the acidic hydrogen, or proton, is attached. Hence, if the above ideas are sound, it follows as a matter of course that each of the substituents  $NO_2$ ,  $CN$ ,  $COR$ , and  $SO_2R$  must exercise some special restraint on the electrons of an attached carbon atom; the case is only one of many covered by scheme 7, in the paper by Allan, Oxford, Robinson, and Smith (J., 1926, 404), in which scheme carbonyl was evidently used to typify all substituents which come in the above category (compare *ibid.*, p. 403, line 8 from bottom). The connexion between electron-restraining properties and meta-directive power had previously been a strong plank in the platform of supporters of "polarity theories" and a passing reference to Robinson's discerning extrapolation from this general basis and his own experiments to the prediction of meta-directive effects in benzylamine salts may serve as a reminder of this. It may therefore be maintained that no date later than that of the paper by Allan, Oxford, Robinson, and Smith may properly be assigned to the complete association of all the above ideas, although much of real novelty has since been written in connexion with the same topics and numerous important extensions have been suggested.

It is, however, not enough to attribute to any given substituent an "inherent" electron-attractive or electron-repulsive power, and then to assume that the apparent contradictions are due to covalency adjustments which are inseparable from a completed chemical

change. The present authors are convinced that the idea of interior electron displacements formulated by Lewis (compare "Valence and the Structure of Atoms and Molecules," G. N. Lewis, American Chemical Society Monographs, 1923), though acceptable in many applications and in particular to the strengths of the hydroxides of the elements as bases and acids (*loc. cit.*, p. 138), does not admit of the extension suggested by Lewis himself in his attempt to account for the high ionisation constants of  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -chloro-derivatives of saturated aliphatic acids (*loc. cit.*, p. 139). A number of workers have accepted the lead given by Lewis on this point; but it may be noted that in certain schools of thought the mass of indications pointing to the existence of some transmission of effects by interior means is ignored and distances of points from poles are calculated apparently on the assumption that the disturbances are propagated solely through the medium (compare Larsson and Holmberg, *Z. anorg. Chem.*, 1929, **183**, 30).

Insufficient attention has been paid to the possibility, already partly recognised, that even in the resting state of a molecule the effect of a substituent at a given point, even at a considerable distance from the substituent, may be the resultant of at least two simultaneous influences, one reaching the point from the exterior and the other from the interior, that is *via* the electronic system of the adjacent atom, the condition of which, in its turn, is likely to be determined by the resultant of interior and exterior influences. The exterior and interior forces at a given point may operate either in harmony or in opposition according to the nature of the substituent, and possibly also according to other circumstances, and obviously may affect one another to a greater or less extent throughout the whole range of collateral transmission.

It is almost certainly erroneous to suppose that the net effect of a substituent, Y, in say,  $Y \cdot CHR_1R_2$ , on the electrons of the carbon atom to which it is directly attached is always in the same sense as its net effect on the electrons of more remote atoms. It so happens that, if attention be restricted to the meta-directive substituents above specified, no glaring discrepancy is revealed, for not only does each of these substituents exercise, in the light of the above ideas expressed in terms of Lewis's theory of proton expulsion, a marked restraining effect on the electrons of any carbon atom to which it is directly attached, but it also displays consistent restraining effects on the electrons of atoms more remote, as shown by the large ionisation constants of all carboxylic acids in which these substituents occur. With a number of other substituents, however, and more especially with some of the powerfully ortho-para directive ones, no such consistency obtains.

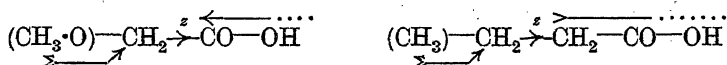
Discussion of even the most elementary issues involved in this complicated question requires a clear understanding as to the implication of terms used. In view of this, the electropolar effect of a substituent is now defined for the present purpose and without references to any particular hypothesis, as that effect which, when the substituent occurs at the  $\alpha$ -,  $\beta$ -,  $\gamma$ - and more remote positions in a saturated aliphatic acid, leads consistently to a rise or consistently to a fall in the ionisation constant of the acid, and diminishes as the distance from the substituent increases. The rate of diminution in the series of saturated fatty acids is given approximately by Derick's logarithmic rule (*J. Amer. Chem. Soc.*, 1911, **33**, 1152).\*

The authors prefer to use the description "electropolar" effect or factor, due to Flürscheim, rather than "electron affinity" (Lewis), because the latter expression has been applied (a) to the restraint which an atom exercises over its own electrons, (b) to interior electron displacements consequent thereon, and (c) to true electropolar effects, which, in the view of the present authors, have often been confused with (b). The description "general polar," originally suggested (1921) as equivalent to Flürscheim's "electropolar," has since been used to specify not only true electropolar effects but also effects of interior electron displacements as conceived by Lewis.

Significant connexions which have appeared from the work of Bjerrum and others between electropolar effects and dipole moments, combined with the circumstances that electropolar effects make themselves felt at considerable distances from their point of origin even when a long saturated chain of carbon atoms intervenes, lead the authors to accept the view that the electropolar effect of a substituent, Y, is essentially the manifestation of a change in the electrical fields immediately exterior to the chains of atoms on the molecule. They imagine that the substitution ordinarily produces a change in the external field which is equivalent to the superposition of a new external field on the original one, and that this superimposed field increases in intensity as the substituent is approached from distant parts of the molecule. At some point, at a very small distance (measured in atomic diameters) from the point of substitution, it is, however, presumed that the superimposed field may be extremely complex, so that neither its intensity nor its sign can be deduced from a knowledge of the distribution of that field at points more remote—or at least not until that knowledge is far more exact than can be claimed at the present time. The precise distance at which the exterior effects may be treated as

\* Admittedly the criterion can strictly be applied only when the influence of "steric" factors has been eliminated.

mathematically separable from the primary and its interiorly transmitted effects is likely to remain as an outstanding difficulty; but on the view advanced by Lapworth and Manske (J., 1928, 2536, 2537) its point must be somewhere *beyond* the atom at which substitution takes place. Assuming, for simplicity, that this point in saturated systems lies immediately beyond the electrons of the atom in question and that "steric" effects may be treated as irregularities in an otherwise regularly diminishing, exterior field beyond this point, the opposite electropolar factors of  $\text{O}\cdot\text{CH}_3$  and  $\text{CH}_3$  may be suggested by the arrows placed above the two figures



To the left of these two upper arrows it is postulated, not that an exterior field is non-existent, but that, whatever its direction may be, it is, by definition (J., 1928, 2536), only one of the factors in the primary effect,  $\Sigma\text{---}\text{CH}_2\text{---}$ , of the substituent on the electrons of the carbon atom to which it is directly attached, and may not be counted twice.

This interpretation of the facts, however, demands that in the two cases just specified, the displacements implied by the  $\text{---}$  signs are very small, which is consistent with remarks which are made later in this paper on transmission by a single bond in a saturated carbon system (p. 450). The sign  $z$  is used to imply that the value,  $>$ , is almost zero.

Proton is admittedly unique; and there is strong physical evidence, largely but not wholly spectroscopic, that proton can enter very deeply into the electronic systems of other atoms (compare Knorr, *Z. anorg. Chem.*, 1923, **129**, 109; Müller, *Z. Elektrochem.*, 1924, **30**, 493; 1925, **31**, 46, 143; Lederle and Rieche, *Ber.*, 1929, **62**, 2576). The presence of hydrogen in direct combination with another non-metallic atom may then be equivalent to an increase in the central restraining charge of that atom, and this would lead, algebraically, to a corresponding decrease in restraint when the hydrogen is replaced. This factor is doubtless not the only one operative, and electrostatic attraction between the nucleus of one atom and the electrons, especially if "unshared," of another atom in the sense of theories previously used by Stark, Robinson, Lapworth and others is consistent with numerous data and is not excluded by electronic theory. It remains, however, as a striking fact that, with the exception of some, like  $\text{NMe}_3^+$ , which themselves contain an additional positive charge, and others, like  $\text{NO}_2$ , which contain a qualitatively equivalent dipole, nearly all the familiar substituents produce, on 3-co-ordinated carbon, chemical effects



which correspond with those to be anticipated from a virtual decrease in the central charge of the carbon atom (compare Lapworth and Manske, J., 1928, 2536). Examples of this include such diverse substituents as  $\text{NH}_2$ ,  $\text{NMe}_2$ ,  $\text{OMe}$ ,  $\text{Cl}$ , and  $\text{Alk}$ , some (*e.g.*,  $\text{Cl}$ ) with electron-restraining and others (*e.g.*,  $\text{Alk}$ ) with electron-releasing electropolar factors.

On the evidence of the ionisation constants of substituted acetic, propionic and butyric acids, the electropolar factors for  $\text{OH}$  and  $\text{O}\cdot\text{CH}_3$  attached to 4-co-ordinated carbon are definitely *electron-restraining*; moreover, *m*-hydroxybenzoic acid is stronger than benzoic acid, and there is strong evidence that the electropolar effect is usually the dominant one in the meta-position (compare, *inter alia*, J., 1929, 2547, lines 7—9). Nevertheless,  $\text{OH}$ , or  $\text{O}\cdot\text{CH}_3$ , when replacing  $\text{H}$  attached to an aromatic nucleus, confers on some electrons of the nucleus a greatly *decreased* restraint; and when  $\text{OH}$  replaces the  $\text{H}$  of the kation,  $\text{H}\cdot\text{CO}_2\ominus$ , of formic acid, the product,  $\text{HO}\cdot\text{CO}_2\ominus$ , has a very greatly increased affinity for proton, connoting a greatly *decreased* restraint on the electrons of the carboxyl oxygens. In these two cases, however, the  $\text{OH}$  has replaced  $\text{H}$  attached to 3-co-ordinated carbon and the view has already been expressed by Lapworth and Manske (J., 1928, 2536), that this occurrence is undoubtedly associated, in the case of  $\text{OH}$ , with a greatly decreased restraint on the carbon electrons, which restraint can be transmitted in turn, by electron displacements (Lewis), to other atoms in the molecule, the intensity and extent of transmission varying very greatly with structural conditions.

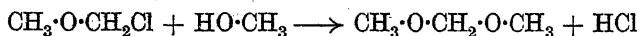
It is perhaps desirable at this juncture to state that the present view accommodates the case of initiation of electron displacement at points remote from the substituent by the operation of the electropolar effect on a plastic system, such as a double bond, a 1 : 3-diene system, or a carbon-halogen linkage. The slight polarisation of the ethylenic linkage in stearolic acid, demonstrated by Robinson and Robinson (J., 1926, 2204), is regarded by the present authors as a case coming within this category; such effects might suitably be called "imported," in contrast to "transmitted."

A 1 : 3-diene, or an aromatic, system, when acted upon either by an imported or a transmitted strain, may display "alternate effects" of several kinds. The problem of the mechanism of "static" alternate effects such as those indicated by study of dissociation constants of aromatic carboxylic acids and cyanohydrins must be approached from the standpoint of a sound theory of the more elementary phenomena associated with substitution.

The question whether a given substituent operates on 4-co-ordinated (or "saturated") carbon in the same mode as it operates

on 3- and 2-co-ordinated carbon was touched on very lightly by Lapworth and Manske, in view of the paucity of convincing evidence bearing thereon (*loc. cit.*, p. 2537). The substituents  $\text{NO}_2$ ,  $\text{CN}$ ,  $\text{COR}$ , and  $\text{SO}_2\text{R}$  offer no difficulty from the qualitative point of view, their primary interior factors (*ibid.*, p. 2536) and electropolar factors being, as previously stated, clearly and consistently electron-restraining, no matter to which type of carbon atom they are attached. It has been shown in the preceding pages that the conjunction of Lewis's theory with the idea of incipient ionisation in the derived systems,  $\text{X}\cdot\text{CHR}_1\text{R}_2$ , implies that these substituents exercise a restraining effect on the electrons of 4-co-ordinated carbon, thus facilitating the removal of the hydrogen atom as proton by suitable acceptors. In the following pages an attempt is made to show that some of the more powerfully ortho-para directive substituents exert precisely the opposite effect on the electrons of directly attached, 4-co-ordinated carbon, so that when the latter is also associated with an atom or group, which either *per se* or by association with a suitable acceptor, can act as an anion, a state of "incipient ionisation" is brought about in the sense opposed to that induced by the meta-directive substituents  $\text{NO}_2$ ,  $\text{CN}$ ,  $\text{COR}$  and  $\text{SO}_2\text{R}$ , when occupying similar positions.

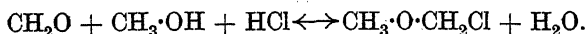
It is well known that the halogen in  $\alpha$ -chloroalkyl oxides such as monochlorodimethyl ether,  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\text{Cl}$ , is exceptionally labile. Contrasting  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\text{Cl}$  with  $\text{H}\cdot\text{CH}_2\text{Cl}$ , it may be said with confidence that the replacement of H by  $\text{O}\cdot\text{CH}_3$  does not lead to any of the results to be anticipated from a virtual increase in the central charge of the carbon atom of the  $\text{CH}_2$  group. Such results would be, for example, a more ready reducibility of the chloro-compound to the hydride, or a tendency to react with water in accordance with the scheme  $\text{R}\cdot\text{Cl} + \text{HOH} \longrightarrow \text{R}\cdot\text{H} + \text{HOCl}$  (compare the properties of  $\text{NCl}_3$  and  $\text{NH}_2\text{Cl}$  with those of chloro-derivatives of methane). On the contrary, there is observed a greatly increased tendency for the halogen atom to appear as chloridion; moreover, the group  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2$  has apparently so small an affinity for its bonding electrons that it can replace proton, even in presence of free hydrochloric acid, as in the facile reaction of the chloride  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\text{Cl}$  with methyl alcohol :



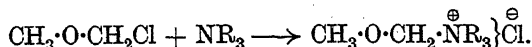
(Henry, *Ber.*, 1893, 26, 933, *Ref.*).

The extraordinary facility of the transformations of this chloride and the consistent relative "polarities" of its two parts,  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2$  and  $\text{Cl}$ , as well as the comparatively small heat changes involved, are well illustrated by its behaviour towards water, alkali and con-

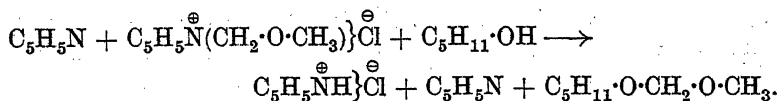
centrated hydriodic acid respectively. In each case hydrolysis occurs quickly, the chloro-ether, at first insoluble, dissolves within a few seconds when shaken vigorously with the cold aqueous liquid. In the case of the strong, aqueous hydriodic acid, the heat display is so small that, with equal volumes of acid and chloro-ether, the rise of temperature is only about 7°. No free iodine is liberated even if the compound is added to the hot acid. From the work of Henry (*loc. cit.*) and others there is good reason to conclude that in each of the three cases the change which takes place is simply a reversal of that on which the ordinary method of preparing the ether is based:



Monochlorodimethyl ether acts almost instantaneously on tertiary bases (Litterschied, *Annalen*, 1901, **316**, 161), forming quaternary salts:



The present authors have observed that although, as found by Litterschied, these salts are also formed almost instantaneously in presence of an alcoholic solvent, such as amyl alcohol or *cyclohexanol*, they may subsequently react with the alcohol on warming in presence of excess of the tertiary base, the methoxymethyl residue evidently leaving the nitrogen atom and replacing the proton of some of the alcohol. Thus with pyridine and amyl alcohol:



It may be worth while to point out that these reactions do not seem to differ in any essential feature from those which occur during the well-known process, due to Einhorn, for acylation of alcohols by means of acyl chlorides and tertiary amines (*Annalen*, 1898, **301**, 95), though the yields obtained are less satisfactory, owing in some cases to less complete reaction and in others to formation of products of higher molecular weight in which methoxyl has been replaced. In both cases quaternary salts are formed in the first instance by direct union of amine and acid chloride (compare Dennstedt and Zimmermann, *Ber.*, 1886, **19**, 75) and there is no sufficient reason to assume that there is an essential distinction between the two mechanisms. The authors infer that both acyl groups and  $\alpha$ -alkyloxymethyl groups can function much as protons do; that is to say, while probably not capable of separate existence in solution as kations, they are readily detached from their bonding

electrons and thus, in the same sense as such protons, occur in the state frequently described as "incipient ionisation."

In the authors' view the conditions which give rise to the modes of reaction of monochlorodimethyl ether are to be regarded as pre-existent in the resting molecules,  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\text{Cl}$ , and it is not necessary to assume complete conversion of the molecules into desmotropic forms prior to interaction with the agents. Oxonium chemistry certainly indicates that reversible changes such as  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\text{Cl} \leftrightarrow \text{CH}_3\cdot\text{O}^+\cdot\text{CH}_2\text{Cl}^-$  might take place readily; but the

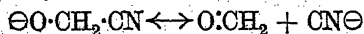
existence of such reversible relations in itself connotes comparatively small free energy differences between the molecular configurations in the two isomeric forms, and such forms are probably subject to similar interior distortions, demanding comparatively small "activation" increments of energy for transformation in either direction. It is on this basis, and not on the hypothesis of one ion common to both forms, that the authors would approach the theory of isodynamic isomerism; the observations of Leuchs (*Ber.*, 1913, 46, 2438) and of Kuhn and Albrecht (*Ber.*, 1927, 60, 1297), with optically active compounds, strongly support the idea that the ions of the so-called "pseudo-acid" forms have individual existence.

The present authors would represent the interior effects which they believe to be produced by the conversion of  $\text{H}\cdot\text{CH}_2\text{Cl}$  into  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\text{Cl}$ , by the strain-symbol,  $\text{CH}_3\cdot\text{O}-\text{CH}_2-\text{Cl}$ , where,

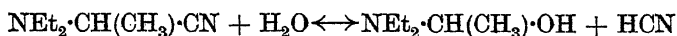
in contrast to the case of  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (p. 444), the transmitted effect is considerable (in the plastic  $\text{C}-\text{Cl}$  bond) and has more influence on the properties of the compound than has the electropolar effect



The extremely variable lability of CN directly attached to carbon seems strongly to support the general ideas above advanced. Ordinarily, CN directly attached to carbon cannot be removed as cyanidion. Even cyanohydrins  $\text{HO}\cdot\text{CR}_2\cdot\text{CN}$  are mostly quite stable in this respect at the ordinary temperature, providing that appreciable ionisation of the hydroxyl hydrogen be prevented, as by addition of a trace of mineral acid (Lapworth, *J.*, 1901, 79, 1268; 1906, 89, 948; Ultée, *Rec. trav. chim.*, 1909, 28, 248, 257); on the other hand, partial breaking down, with attainment of equilibrium, takes place extremely quickly at the ordinary temperature if the conditions are on the alkaline side, thus permitting of a small amount of ionisation of the acidic cyanohydrin (*J.*, 1904, 85, 1206):



The instability of  $\alpha$ -amino-nitriles is well known, and the authors have observed that the compound  $\text{NEt}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CN}$  decomposes at the ordinary temperature in presence of water; free hydrogen cyanide is formed and if this be allowed to escape from the system complete decomposition takes place ultimately at the ordinary temperature. The reactions involved are again reversals of those followed during the ordinary method of preparing the compound:



(not necessarily by way of the desmotropic form  $\text{NEt}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{CN}^\ominus$ ).

The compound  $\text{NEt}_2\cdot\text{CH}(\text{CH}_3)\cdot\text{OH}$  then breaks down much in the same way as a cyanohydrin does, giving  $\text{NEt}_2$  and  $\text{CH}(\text{CH}_3)\cdot\text{O}$ . The case of cyanodihydroberberine is closely comparable with this (compare Robinson and Robinson, J., 1917, 111, 966).

Compounds having the structure  $\text{CH}_3\cdot\text{O}\cdot\text{CR}_1\text{R}_2\cdot\text{CN}$ , unlike cyanohydrins themselves and unlike  $\alpha$ -amino-nitriles, are exceedingly stable compounds, and do not yield their cyanidion under most drastic treatment.

It seems clear, therefore, that in respect to their efficiencies in promoting the withdrawal of CN from the same carbon atom, the order of four important substituents is  $\ominus\text{O}$ ,  $\text{NAlk}_2$ ,  $\text{OH}$ ,  $\text{O}\cdot\text{CH}_3$ . The last of these is here quite ineffective, and even  $\text{OH}$  is usually effective only at temperatures above the ordinary, in which circumstances almost any ketone cyanohydrin can lose hydrogen cyanide; menthone cyanohydrin when exposed cannot be prevented from doing so slowly even at the ordinary temperature and in presence of stabilising hydrogen chloride (Lapworth, Manske, and Robinson, J., 1927, 2054). It may be noted that the order of the four substituents above deduced is the same as that accepted for ortho-para directive powers, which order, however, is not necessarily always the same as that for "static" or average primary effects. Aromatic substitution, as Robinson has constantly maintained, is no doubt very largely a phenomenon connected with specially energised molecules in the system and not with the average molecules, and the nitroso-group affords a striking example of a substituent the "static" primary effect of which on carbon is in one sense (electron-restraining, like  $\text{CO}\cdot\text{R}$  or  $\text{NO}_2$ ) and nevertheless does not too effectively oppose the formation of energised forms in which it is in effect operating in the opposite sense (ortho-para directive and electron-releasing) (compare Robinson, *Chem. and Ind.*, 1925, 456). Such an associated function may be termed a "permissive" property of the substituent.

When alcoholic potassium cyanide acts on polynitro-derivatives

of the aromatic series, the group  $\text{O}\cdot\text{CH}_3$  enters the molecule at the carbon atom from which the  $\text{NO}_2$  radical is displaced; the group  $\text{CN}$ , when it enters, is found on a carbon atom to which  $\text{H}$  was originally attached (Bruyn and others; compare Kenner, J., 1914, 105, 2730). The opposite primary interior effects of  $\text{O}\cdot\text{CH}_3$  and  $\text{CN}$  are doubtless here foreshadowed or utilised in some way at intermediate stages,



$\ominus\text{NO}_2$  being "loosened" in the former case and  $\oplus\text{H}$  in the latter (compare "Summary" of present paper).

On considering all the evidence now available it seems clear that the statement made by Lapworth and Manske to the effect that the influence of substituents on 4-co-ordinated carbon is "certainly small" (J., 1928, 2537) was unfortunate, and a more accurate statement would have been that the changes produced by substitution of  $\text{H}$  attached to 4-co-ordinated carbon are "certainly more difficult to detect" than with 3-co-ordinated carbon.

This difficulty seems to be due in the main to the circumstance that changes in the restraint on the electrons of 4-co-ordinated carbon are transmitted, if at all, only to a very feeble extent to another carbon atom; thus even the considerable effect of the substituent  $\text{O}\cdot\text{CH}_3$ , which is manifest in the properties of  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\text{Cl}$ , does not suffice to cause loss of the  $\text{CN}$  group from  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{CN}$  or  $\text{CH}_3\cdot\text{O}\cdot\text{CH}(\text{CH}_3)\cdot\text{CN}$  (compare Robinson, on resistance offered by a saturated carbon atom, *Chem. and Ind.*, 1925, 118).

Owing to the difficulty of detection and comparison of static primary effects on 4-co-ordinated carbon, except in special cases such as those above discussed, it would be premature to maintain that the sequence of substituents in this connexion is the same as the sequence for static primary effects on 3-co-ordinated carbon. On *a priori* grounds it would seem possible that such might be the case, at least for substituents which contain no double-bonded structure adjacent to the point of attachment. Comparison of the properties of  $(\text{Cl})\cdot\text{CH}_2\text{Cl}$  and  $(\text{CH}_3)\cdot\text{CH}_2\text{Cl}$  with those of  $(\text{H})\cdot\text{CH}_2\text{Cl}$  clearly indicates that the "primary" influence of  $\text{Cl}$  or  $\text{CH}_3$  on 4-co-ordinated carbon is very much smaller than that of  $\text{O}\cdot\text{CH}_3$ , and this again is broadly in agreement with effects already deduced on 3-co-ordinated carbon. Whatever may transpire hereafter, it now seems beyond reasonable doubt that when substituents are arranged in the order of their "static" (or average) primary effects on directly attached, 4-co-ordinated carbon, that order will

be quite different from the electropolar sequence (order of "electron affinities") and will correspond much more closely with Flürscheim's "quantitative" sequence, though, as already explained (p. 449), with certain modifications connected with the mechanism of aromatic substitution. It is doubtful whether the precise order, even if there be such, for static primary effects of substituents can be deduced from chemical reactions, but the authors assume that facile and reversible reactions provide the most trustworthy indications. The study of equilibrium constants furnishes a basis for comparing average free energies over a large number of molecules; but "primary" effects are not the only factors involved.

There is yet another complication, as there is reason to believe that with certain substituents which have comparatively small primary effects, even the sense of their primary effects is not wholly independent of the nature of the other substituents present on the same atom. Thus the successive replacement of hydrogen atoms in ammonia by methyl groups causes at the first step a rise and at the last a fall in the basic affinity constant. Again the capacity of the  $\text{CCl}_3$  group to pass, together with its bonding electrons, from one state of combination to another (as from proton in chloroform to depleted carbon in acetone) suggests that the joint primary (*i.e.*, totalised) effect of the three chlorine atoms on the carbon is electron-restraining, whereas the primary effect of Cl on carbon of the aromatic nucleus or of carbonyl appears consistently electron-releasing (compare J., 1928, 2547); on the other hand, a "permissive" effect might be concerned here.

## Section II.

This section deals only with observations of which a more detailed account than has been given in the preceding pages seems desirable.

(1) *Action of Methoxymethylpyridinium Chloride on Hydroxy-compounds.*—(a) *Benzyl alcohol.* Chlorodimethyl ether (40 g.) was slowly added to purified pyridine (100 c.c.) dissolved in dry ether (500 c.c.) cooled in ice-water, the crystalline quaternary salt which at once separated being then collected rapidly on a Buchner funnel, washed with ether, and transferred to a dry flask. A small sample of the chloroplatinite was prepared and had m. p.  $180\text{--}182^\circ$  (efferv.) (compare Litterschied, *Annalen*, 1901, **316**, 168). The bulk of the salt was heated with dry benzyl alcohol (54 g.) and pyridine (80 c.c.) at  $90\text{--}95^\circ$  for 6 hours, after which time addition of ether to a sample of the cooled mixture led to precipitation of pyridine hydrochloride (chloroplatinite, m. p.  $238\text{--}240^\circ$ ). In working up the product, the latter was cooled and mixed with water, made slightly acid, and extracted twice with ether (400 c.c. in all), which was then washed

with dilute hydrochloric acid and water successively, dried over sodium sulphate, and evaporated. From the residual liquid, a main portion (40 g.), b. p. 205—215°, and a less volatile portion (5 g.) were obtained. To remove benzyl alcohol, the former was shaken repeatedly with a concentrated aqueous solution of sodium salicylate\* until it suffered no further appreciable diminution in bulk and was then refractionated. A fraction (25 g.), b. p. 208—211°, was obtained, consisting of *methoxymethyl benzyl ether*,  $C_6H_5 \cdot CH_2 \cdot O \cdot CH_2 \cdot O \cdot CH_3$ .

The ether is obtained in better yield (about 36 g.) by simply mixing benzyl alcohol (54 g.), chlorodimethyl ether (40 g.), and dry pyridine (50 g.) slowly but without special cooling, and working up the product as before. It is a colourless oily liquid, b. p. 208—211°/756 mm., having a fragrant fruity odour (Found: C, 70.8; H, 7.9.  $C_9H_{12}O_2$  requires C, 71.1; H, 8.0%).

In each of the following cases, the alcohol was warmed with the mixture of chlorodimethyl ether and pyridine for several hours, and the product worked up as above.

(b) *cycloHexanol*. The yield of *methoxymethyl cyclohexyl ether* was so poor that a homogeneous product could not be isolated. Most of the alcohol was recovered unchanged, and from 50 g. of *cyclohexanol* only 1.8 g. of oil (b. p. 190—210°) were obtained (Found: C, 67.3; H, 11.2.  $C_8H_{16}O_2$  requires C, 66.6; H, 11.2%). About 2.5 g. of higher-boiling product (b. p. 255—274°) accompanied this.

(c) *sec.-β-Octyl alcohol*. From 65 g. of this alcohol were obtained 5 g. of *methoxymethyl sec.-octyl ether*, as a liquid with a fragrant odour; b. p. 188—190° (Found: C, 69.2; H, 12.7.  $C_{10}H_{22}O_2$  requires C, 69.0; H, 12.6%).

(d) "*Amyl alcohol*." A commercial amyl alcohol, b. p. 131—132°, being used (44 g.), a fraction representing *methoxymethyl "amyl" ether* was obtained in fair yield (15 g.). This product had a very powerful, not unpleasant odour, reminiscent of amyl alcohol (Found: C, 63.5; H, 12.2.  $C_7H_{16}O_2$  requires C, 63.6; H, 12.7%).

The action of *methoxymethylpyridinium chloride* on amyl alcohol appears to be much less energetic than on benzyl alcohol. In the latter case the heat disengaged in admixture is sufficient to ensure completion of the reaction, but in the former it was found that most of the amyl alcohol is recovered unchanged unless the mixture is heated on the steam-bath before it is worked up. No special trials were made to find the minimum time necessary.

(e) *Phenol*. No reaction appeared to take place with the quater-

\* A solution of sodium salicylate seems to have been used in industry for the separation of alcohols from mixtures of these with non-alcoholic compounds.



nary pyridinium salt, and no neutral product boiling above 100° was detected. A sample of the recovered phenolic material was carefully fractionated in order to ascertain whether any alkylation in the nucleus had taken place, but nothing boiling appreciably higher than phenol could be isolated. The expected ether,  $C_6H_5 \cdot O \cdot CH_2 \cdot O \cdot CH_3$  boils at 188—189°/760 mm. (compare *Centr.*, 1909, I, 1681).

This inertness of phenol is doubtless associated with its acid character, having a parallel in the difficulty which is experienced in the alkylation of nitrophenols or carboxylic acids by means of aqueous alkali and methyl sulphate.

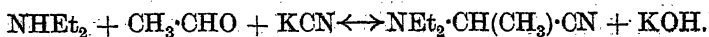
The order of the hydroxy-compounds examined as to the facility with which they react with methoxymethylpyridinium chloride appears to be: benzyl alcohol, amyl alcohol, *sec.*-octyl alcohol, cyclohexanol, phenol, and a close relation with the order of their acidities may be suspected.

(2) *Observations on some  $\alpha$ -Substituted Nitriles.*—(a)  *$\alpha$ -Diethylaminopropionitrile.* This compound, which has already been made by Klages (*J. pr. Chem.*, 1902, **65**, 196), is readily produced by slowly mixing diethylamine with a slight excess of acetaldehyde and liquid hydrogen cyanide in the required proportion. There is considerable heat development and careful cooling is therefore necessary. The product, after exposure in a vacuum for a short time, forms a mobile liquid, stable in absence of water at the ordinary temperature (Found: N, 21.9. Calc. for  $C_7H_{14}N_2$ : N, 22.2%).

A sample so prepared was added to a solution of silver nitrate acidified with nitric acid and yielded silver cyanide corresponding with 1.3% of free hydrogen cyanide, the nitrile itself (or rather its salt) being stable to this reagent. The total CN present in the same sample was determined by shaking with excess of dilute sodium hydroxide solution and silver hydroxide and then adding excess of dilute nitric acid. The total CN found was 23.1%; hence the combined CN was 21.8% (theory requires CN, 20.4%).

On distillation of the nitrile under reduced pressure, a portion, b. p. 72—77°/17 mm., amounting to about at least 60% of the whole is obtained. This appears to consist mainly of the original nitrile, but is decidedly more viscous, and some decomposition products are probably present.

The nitrile can also be obtained, though in smaller yield (about 30% of the theoretical), by adding diethylamine and acetaldehyde in equimolecular proportion to a concentrated aqueous solution of potassium cyanide and extracting the product with a large bulk of ether. Here potassium hydroxide must be formed:



When the amino-nitrile is left with water, the odour of hydrogen cyanide becomes perceptible within a few minutes. If the hydrogen cyanide formed is continuously removed by exposure of the vessel in a vacuum desiccator over a solution of sodium hydroxide, the layer of oily nitrile gradually disappears and, after several days, only a scum of tarry product can be seen on the surface of the water, though even then a faint odour of hydrogen cyanide is perceptible.

The picrate is best made from the nitrile before distillation, a solution of picric acid in cold dry ether being used. It is deposited as long prisms, m. p.  $99.5-102^\circ$ ; Klages (*loc. cit.*) gives m. p.  $102^\circ$ . As its melting point was appreciably lowered by recrystallisation, the crude salt was analysed (Found: C, 44.2; H, 4.8; N, 22.3, 19.7. Calc. for  $C_{13}H_{17}O_7N_5$ : C, 43.9; H, 4.8; N, 19.7%).

(b) *Methoxyacetoneitrile*. This was made by the method of Polstorff and Meyer (*Ber.*, 1912, 45, 1911) from formaldehyde, potassium cyanide, and methyl sulphate. Its identity was confirmed by its boiling point ( $120-122^\circ$ ) and other properties (Found:  $CH_3 \cdot O$ , 42.7. Calc. for  $CH_3 \cdot O \cdot C_2H_2N$ :  $CH_3 \cdot O$ , 43.6%), as well as by the properties and composition of the methoxyacetamide prepared from it; needles, m. p.  $96.5-97^\circ$  (Found:  $CH_3 \cdot O$ , 34.8. Calc. for  $CH_3 \cdot O \cdot C_2H_4ON$ :  $CH_3 \cdot O$ , 34.8%).

The nitrile does not yield detectable traces of hydrogen cyanide or metallic cyanide when heated alone, with alkalis, with solid sodium hydroxide at its boiling point, with potassium in boiling toluene, or with silver nitrate and dilute nitric acid.

(c) *Methoxypropionitrile*. This compound is most readily made by the method used by Polstorff and Meyer in preparing the lower homologue, the formaldehyde being replaced by an equivalent amount of acetaldehyde. It has previously been made by Gautier from the corresponding chloro-ether (*Ann. Chim. Phys.*, 1909, 16, 315).

The product obtained by the present authors had b. p.  $128-130^\circ/758$  mm. (Found:  $CH_3 \cdot O$ , 30.0. Calc. for  $CH_3 \cdot O \cdot C_3H_4N$ :  $CH_3 \cdot O$ , 30.1%). It was readily converted into the corresponding amide (needles, m. p.  $83^\circ$ , from light petroleum) by means of alkaline hydrogen peroxide. It yielded no hydrogen cyanide nor metallic cyanide under the most drastic treatment.

### Summary.

The electron displacement theory of G. N. Lewis, in its application to phenomena associated with results of introducing substituents into the molecules of carbon compounds, is accepted only in part.

It is shown that there is good reason to believe that the substituents  $\ominus O$ ,  $NAlk_2$ ,  $OH$  and  $O \cdot CH_3$ , in descending order of

efficiency, greatly increase the electron fugacity of directly attached, 4-co-ordinated carbon, and thus form a group in complete contrast to the carbonyl and nitro-radicals.

There is no simple relation between such effects ("primary" effects) and the so-called electron affinities ("electropolar" factors) of substituents. There is a close general connexion, however, between the former and the ortho-para directive powers ("quantitative" factors).

The tendency of a radical to enter into combination with a given carbon atom or/and to replace another radical attached thereto, is influenced not only by the nature of the radicals already attached to the carbon atom but also by those properties of the entrant radical which determine what the sign and the magnitude of the "primary" effect of that radical will be after such combination has taken place.

Evidence is cited that, at least with a substituent which has a comparatively small "primary" effect, even the sign of that effect is not always independent of the nature of the other radicals attached to the atom.

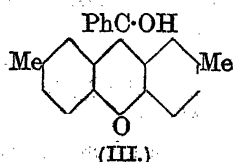
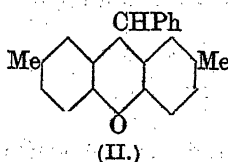
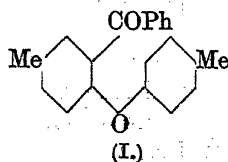
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## LXI.—*Substituted Diaryl Ethers. Part III. A New Synthesis of Substituted Xanthhydryls.*

By JOSEPH REILLY and PETER J. DRUMM.

IN a recent communication (J., 1927, 2814) the authors showed that di-*p*-tolyl ether yields only monosubstituted derivatives in the Friedel-Crafts reaction. The product of interaction of benzoyl chloride and di-*p*-tolyl ether was assigned the constitution of an ortho-substituted diaryl ether (I) because it was converted into 9-phenyl-2:7-dimethylxanthen (II) and also because its solutions in acetic and sulphuric acids were yellow, indicating xanthhydryl formation through ring closure. The non-formation of a phenyl-hydrazone was attributed to steric hindrance by the tolyloxy-radical in the ortho-position to the carbonyl group. The supposed ketone (I) has now been found to be the isomeric 9-phenyl-2:7-dimethylxanthhydryl (III), which has also been obtained by the action of magnesium phenyl bromide on 2:7-dimethylxanthone.



This interaction constitutes a simple method of producing substituted xanthhydrols in good yield from readily accessible materials. Ordinarily, xanthhydrols are prepared from the corresponding xanthenes by the Grignard reaction (compare Ullmann and Engi, *Ber.*, 1904, **37**, 2370). This method is unsuitable in the case of the above xanthhydrol, since the preparation of 2 : 7-dimethylxanthone from *p*-cresotic acid is not satisfactory.

9-Phenyl-2 : 7-dimethylxanthhydrol, when boiled with acetic acid, gave 9-phenyl-2 : 7-dimethylxanthen (*loc. cit.*), which was also prepared by Feuerstein and Lipp (*Ber.*, 1902, **35**, 3255) by distillation of 6 : 6'-dihydroxy-3 : 3'-dimethyltriphenylmethane. In Part II (J., 1927, 2815) it was suggested that Feuerstein and Lipp's compound might be a fluorene on the ground that acetic acid is not usually a reducing agent. The xanthen constitution is more in line with the experimental facts, reduction of the xanthhydrol having been brought about by the presence of reducing agents in the acetic acid used : reduction does not take place with specially purified acid. The constitution assigned by Feuerstein and Lipp was confirmed by the re-conversion of their 9-phenyl-2 : 7-dimethylxanthen into the corresponding xanthhydrol by oxidation with lead peroxide.

It has been shown by Schmidlin and Garcíá Banús (*Ber.*, 1912, **45**, 3188) that triphenylcarbinol is readily reduced to triphenylmethane by heating with alcoholic sulphuric acid, and Kauffmann and Pannwitz (*ibid.*, p. 766) have shown that a similar reduction takes place by boiling with alcoholic hydrogen chloride. The present authors have obtained similar results with these reagents in the case of 9-phenyl-2 : 7-dimethylxanthhydrol and comparative experiments have shown that the latter is reduced much more readily than triphenylcarbinol. Formic acid also is an effective but less vigorous reducing agent.

By the action of hydrogen chloride on 9-phenylxanthhydrol in chloroform solution, Bünzly and Decker (*Ber.*, 1904, **37**, 2935) obtained a coloured chloride. With hydrogen chloride, 9-phenyl-2 : 7-dimethylxanthhydrol forms a coloured *chloride hydrochloride* which readily loses a molecule of hydrogen chloride, giving the colourless chloride (compare Gomberg and Cone, *Annalen*, 1909, **370**, 142). Work on the application of the above synthesis to the preparation of substituted thioxanthhydrols is in progress.

#### EXPERIMENTAL.

*9-Phenyl-2 : 7-dimethylxanthhydrol.*—Finely powdered 2 : 7-dimethylxanthone (6 g.) was gradually added to a cooled solution prepared from bromobenzene (10 g.), magnesium (1 g.), and anhydr-

ous ether (50 c.c.). A vigorous reaction ensued and a yellow magnesium double compound separated. After addition of benzene (10 c.c.) the mixture was heated on a water-bath for 1 hour. The solvent was removed, and the residue decomposed by careful addition of ice-cold water. Just sufficient dilute sulphuric acid was then added to dissolve basic magnesium salts. On addition of alcohol to the mixture the precipitated oil quickly solidified (yield, 6.2 g.). The product was crystallised from ethyl alcohol-ethyl acetate, 9-phenyl-2:7-dimethylxanthhydrolyd being obtained in colourless rhombohedra which, alone or when mixed with the product of interaction of benzoyl chloride and di-*p*-tolyl ether, melted at 185—186°.

*4'-Diethylamino-9:9-diphenyl-2:7-dimethylxanthen.*—Diethyl-aniline (1 g.) and 9-phenyl-2:7-dimethylxanthhydrolyd (1 g.) were heated under reflux in acetic acid solution for 30 minutes. The product, which separated on cooling, was obtained from alcohol-ethyl acetate in colourless needles, m. p. 183—184° (Found by the micro-method: C, 85.5; H, 7.0.  $C_{31}H_{31}ON$  requires C, 85.9; H, 7.1%). *4'-Diethylamino-9:9-diphenyl-2:7-dimethylxanthen* is readily soluble in chloroform and ethyl acetate and slightly soluble in ethyl alcohol.

*9-Phenyl-2:7-dimethylxanthhydrolyd chloride hydrochloride* was obtained on saturating a solution of 9-phenyl-2:7-dimethylxanthhydrolyd in anhydrous ether (containing a few drops of acetyl chloride) with dry hydrogen-chloride. It separated slowly in well-defined, reddish-orange prisms, m. p. 147—149° (Found: Cl, 20.3.  $C_{21}H_{17}OCl.HCl$  requires Cl, 19.9%). The chloride hydrochloride is readily soluble in chloroform and acetic acid and insoluble in benzene and ether. It is very susceptible to traces of moisture, being decomposed immediately by water. Heated in a vacuum over quicklime at 130°, it loses a molecule of hydrogen chloride, giving the colourless chloride (Found:  $HCl$ , 10.8. Calc. for  $C_{21}H_{17}OCl: HCl$ , 10.2%). The latter is very unstable, turning red on exposure to air. Its double salt with ferric chloride is identical in all respects with the *ferrichloride* prepared from 9-phenyl-2:7-dimethylxanthhydrolyd by addition of anhydrous ferric chloride to a solution of the xanthhydrolyd in glacial acetic acid previously saturated with hydrogen chloride, which crystallised from glacial acetic acid, containing hydrogen chloride, in reddish-orange rectangular plates, m. p. 181° (Found: Cl, 30.0.  $C_{21}H_{17}OCl.FeCl_3$  requires Cl, 29.4%). It is stable in the air (not showing any signs of decomposition after 2 days), but is slowly decomposed by cold, and more readily by hot water. It dissolves readily in chloroform, nitrobenzene and acetone, but is sparingly soluble in cold acetic acid and insoluble in benzene

and ether. The mercuric chloride and gold chloride double salts were prepared in a similar manner, the former consisting of reddish prisms soluble in chloroform and the latter of golden-yellow needles.

Addition of a solution of bromine in acetic acid to a solution of the xanthhydrol in the same solvent saturated with dry hydrogen bromide gave a precipitate of the tribromide, which formed short reddish-orange prisms, m. p. 145–146° (decomp.) (Found: Br, 46.1.  $C_{21}H_{17}OBr_3$  requires Br, 45.7%). The tribromide is readily soluble in chloroform, nitrobenzene and acetone, but is sparingly soluble in benzene and ether. Water slowly decomposes it with regeneration of the carbinol base.

*9-Phenyl-2:7-dimethylxanthen.*—Zinc dust was gradually added to a boiling solution of 9-phenyl-2:7-dimethylxanthhydrol (1 g.) in 80% acetic acid (50 c.c.). At first a reddish-orange solution was obtained, the colour of which was completely discharged after 10 minutes' boiling. The solid which separated from the hot filtrate was obtained from glacial acetic acid in colourless needles, which melted, alone or when mixed with the 9-phenyl-2:7-dimethylxanthen of Feuerstein and Lipp (*loc. cit.*), at 195–196°. Contrary to the statement of these authors, sulphuric acid in contact with the above xanthen does not develop a yellow colour. On heating, however, a yellow solution with a green fluorescence is obtained, owing probably to partial oxidation of the xanthen to the xanthhydrol by the acid.

*Oxidation of 9-Phenyl-2:7-dimethylxanthen.*—To a hot solution of the xanthen (3 g.) in 80% acetic acid (100 c.c.) was added, during 1 hour, with stirring, freshly prepared lead peroxide (1 mol.) made into a paste with acetic acid. The solution, at first colourless, gradually assumed a deep orange colour. The solid obtained on dilution of the filtrate with water was collected, washed with hot water, dried, and redissolved in glacial acetic acid. The ferri-chloride was identical with that from 9-phenyl-2:7-dimethylxanthhydrol.

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## LXII.—Photomicrographic Methods applied to Two-component Salt Mixtures.

By WALTER MATTHEW MADGIN.

DISCUSSING the deduction of the type of a two-component system, Freeth (*J. Physical Chem.*, 1925, 29, 497) states that the methods of thermal analysis are not conclusive in many cases. Such methods

would be expected to be most inconclusive in systems where the melting point of each component is lowered by addition of the second component and where the solids are wholly or partially miscible: in both of these systems cooling curves may be misleading, *e.g.*, when the rate of cooling is too rapid and gives rise to cored structure, and the systems may be mistaken for simple eutectic systems. The very successful application of photomicrographic methods to the study of metallic alloys suggests that similar methods might be of value in the cases discussed above, and, in fact, Schemtschuschny (*Z. anorg. Chem.*, 1908, 57, 267) has thereby obtained useful data as to the miscibility or otherwise of potassium chloride with potassium chromate, potassium dichromate, or silver chloride.

From the results of thermal analysis, Guthrie (*Phil. Mag.*, 1884, 17, 462) concluded that the salt pair potassium nitrate-lead nitrate formed a simple eutectic system, but he did not prove the non-existence of limited solid miscibility. Accordingly a photomicrographic study of this system has been undertaken, and the results afford confirmation of Guthrie's. In addition, they point to the conclusion, which would be difficult to deduce from thermal data, that the components of the system show little or no solid miscibility.

Pure lead nitrate is not fusible without decomposition, but with potassium nitrate it forms fusible mixtures of low melting point which are stable provided they do not contain more than 70% of lead nitrate (Guthrie, *loc. cit.*). The melting point of this limiting mixture is given as 335°, which is therefore the highest working temperature permissible and is practically the melting point of pure potassium nitrate (330°; Briscoe and Madgin, J., 1923, 123, 1608). This restricted working temperature is an important consideration when synthetic mixtures are being prepared as described below.

#### EXPERIMENTAL.

The materials used were supplied as of pure quality and were recrystallised until analysis showed at least 99.9% purity.

Mixtures of potassium nitrate and lead nitrate in various proportions and cast in a suitable form for polishing were prepared in ordinary glass test-tubes ( $\frac{5}{8}$ " diameter) by weighing an amount of lead nitrate in a tube and adding a weighed amount of potassium nitrate, which was always on top of the lead salt. The test-tube was placed in an electric heater similar to that described by Briscoe and Madgin (*loc. cit.*) but sufficiently large to cover most of the tube. By this procedure no decomposition of lead nitrate ever occurred,

since the temperature never exceeded  $335^{\circ}$ , and no lead nitrate could ever be left undissolved, being always below the potassium nitrate.

When complete fusion had occurred, the heater was slowly cooled by altering the external resistance, and the rate of cooling was adjusted so as to secure the growth of large crystals. The composition of the various mixtures used is shown below as % of potassium nitrate by weight, No. 4 being the eutectic mixture:

Mixture No. ....	1	2	3	4	5
KNO <sub>3</sub> , % .....	89.6	77.8	65.5	48.6	35.9

Mixtures at or near the eutectic composition (Nos. 3, 4, and 5) required very slow cooling, *viz.*,  $10^{\circ}$  per hour, in order to yield moderately large crystals. Nos. 1 and 2 were cooled much more rapidly, being completely solidified in one hour (a fall of  $130^{\circ}$ ); otherwise the primary crystals of potassium nitrate were much too large and the enclosed eutectic solid was difficult to detect.

The eutectic composition given above differs slightly from that given by Guthrie (*loc. cit.*) and was therefore redetermined as a preliminary to the present work. Further details of this determination will be published elsewhere.

The solidified mixtures obtained as described above were of such an amount as to fill the test-tubes to a depth of 1 inch. After removal from the test-tubes, the castings were sawn into pieces about  $\frac{1}{2}$ " in length and the fresh-cut surfaces were polished.

*Polishing of Specimens.*—The surfaces were filed smooth, rubbed on emery cloth, and then on three grades of emery paper of increasing fineness. This gave a moderate polish but left scratches readily visible under the microscope; further polishing was therefore done on Selvyt cloth on a rotating wheel.

The result of these various treatments was a highly polished but flowed surface, with little or no structure visible, and as ordinary etching reagents could not be employed to remove this surface, 96% alcohol was tried (compare Schemtschuschny, *loc. cit.*). Polished specimens were placed in warm 96% alcohol for about 1 minute, then removed and repolished on the Selvyt cloth. Two or three repetitions of this treatment gave a highly polished surface which showed the structure of the specimen very clearly when examined under the microscope with vertical illumination. It was concluded that the small amount of water in the alcohol had been sufficient to remove the flowed surface and etch lightly the surface beneath.

Microscopic examination showed the existence of two distinct crystalline substances, one white and the other dark grey. Since the specimens were white, this difference is attributed to alteration





FIG. 1 ( $\times 50$ ).  
89.6%  $\text{KNO}_3$ .



FIG. 2 ( $\times 50$ ).  
36%  $\text{KNO}_3$ .



FIG. 3 ( $\times 100$ ).  
48.6%  $\text{KNO}_3$ .



FIG. 4 ( $\times 100$ ).  
36%  $\text{KNO}_3$ .

[To face p. 460.]

cooling between two plane glass surfaces, where complex capillary forces would exist, and this does not provide a convenient method for examining structure.

*Results.*—The photomicrographs show that potassium nitrate and lead nitrate mixtures containing between 89.6% and 36% of the former afford no evidence of solid miscibility and form a eutectic system; banded eutectic structure is easily recognisable in all cases, and staining with hydrogen sulphide enables the two components to be differentiated readily. However, the possibility of partial solid miscibility is not excluded in mixtures of compositions outside the above range. Mixtures containing less than 36% of potassium nitrate would have melting points above 335° and therefore could not be examined. On the other hand, microscopic examination of specimens containing 93, 96, and 98% of potassium nitrate showed the presence of the usual eutectic structure in all cases and, after the specimens had been stained with hydrogen sulphide, the presence of banded eutectic areas between large primary crystals was much more easily recognisable. The photomicrographs of these specimens are not included, as they did not show any fundamental differences from the specimens illustrated.

The stained specimens (Figs. 5, 6, and 7) provide valuable evidence of the absence of solid miscibility. If solid lead nitrate was in any way miscible with potassium nitrate, lead sulphide staining should penetrate throughout the white crystals of potassium nitrate. The absence of such penetration (*e.g.*, Fig. 5) is evidence that the two components are immiscible in the solid state.

Figs. 2, 4, and 7 show that lead nitrate, the constituent in excess, tends to form dendrites much more than potassium nitrate appears to do. It is seen in Fig. 4 that the primary crystals of lead nitrate are surrounded by dark-coloured bands which do not appear to contain any of the lead salt. According to Huntington and Desch (*Trans. Faraday Soc.*, 1908, 4, 51) this phenomenon is due to segregation, large crystals growing at the expense of small crystals when both are in contact with a saturated solution, and it may be in some way related to the tendency of lead nitrate to exhibit dendritic growth. Similar phenomena were not observed in mixtures containing excess of potassium nitrate. It was thought that the formation of these bands surrounding primary crystals might be the outcome of supercooling, since Guthrie (*loc. cit.*) has shown that the eutectic mixture and also those mixtures containing excess of lead nitrate exhibit pronounced supercooling, whereas mixtures containing excess of potassium nitrate do not manifest such supercooling. However, Lamplough and Scott (*Proc. Roy. Soc.*, 1914, 90, A, 600) have confirmed the conclusions of Huntington and Desch.

and have shown that these bands surrounding primary crystals may be formed without supercooling and may be absent when supercooling occurs.

*Summary.*

(1) A method of preparing etched and polished surfaces of mixtures of lead and potassium nitrates is described, and such surfaces are illustrated by photomicrographs.

(2) Hydrogen sulphide reacts with the lead nitrate in these mixtures, and in the photomicrographs the resulting lead sulphide enables the structure to be seen very clearly.

(3) It is concluded that solid potassium nitrate and lead nitrate are completely immiscible when the former exceeds 35% by weight in any mixture. Mixtures containing more than 65% of lead nitrate cannot be investigated.

(4) The results are in agreement with Guthrie's thermal analysis of the same system.

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### LXIII.—*The Interaction between Alkyl Grignard Reagents and Antimony Trichloride.*

By WILFRED JAMES CECIL DYKE, WALTER CULE DAVIES, and  
WILLIAM JACOB JONES.

ON treating magnesium ethyl bromide in ethereal solution with excess of antimony trichloride, Auger and Billy (*Compt. rend.*, 1904, 139, 599) obtained a mixture which they supposed to contain ethyl-dichloro- and -dibromo-stibine. Using equivalent weights of magnesium, methyl iodide, and antimony trichloride, Hibbert (*Ber.*, 1906, 39, 160) prepared trimethylstibine (which he isolated as dibromide representing a yield of 60–70%), together with high-boiling by-products, which were not further examined. Subsequently, Hibbert's method was employed both by Hantzsch and Hibbert (*Ber.*, 1907, 40, 1512), and by Morgan and Yarsley (*J.*, 1925, 127, 184), who devised a special form of apparatus in which the trimethylstibine was purified by distillation of its dibromide with zinc in an inert atmosphere. Morgan and Yarsley also used triethyl- and tri-*n*-butyl-stibine in attempts to prepare bisalkylstibinedichloroplatinums, but they do not describe the properties of the butylstibine. The reactions of the substituted chloro- and iodo-stibines with alkyl Grignard reagents have been investigated by Grüttner and Wiernik (*Ber.*, 1915, 48, 1484, 1759), by Grüttner and

Krause (*Ber.*, 1916, 49, 437), and by Ingold, Shaw, and Wilson (*J.*, 1928, 1283).

The purpose of the present work was twofold, *viz.*, (1) to investigate the character and yields of products other than tertiary stibines, and (2) to characterise the tertiary stibines and investigate their general properties.

In all cases hydrocarbon, formed by the synthetic action of the magnesium on the alkyl bromide, was isolated by exhaustively treating the first runnings, obtained in the isolation of the stibine, with concentrated sulphuric acid.

No evidence of any considerable formation of alkylhalogenostibine, such as that supposed by Auger and Billy (*loc. cit.*), was obtained. Moreover, no higher-boiling product than the stibine (compare Hibbert, *loc. cit.*) was produced in appreciable amount, except the stibine oxide, which, in spite of careful exclusion of air, was always formed to a slight extent.

Interaction between alkyl Grignard reagents and antimony trichloride is always accompanied by separation of finely divided antimony. Direct experiment has proved that on mixing alkylstibines with antimony trichloride there is immediate reduction to antimony.

The total yield of stibine in a preparation, determined iodometrically (see Experimental), was generally 60–70% of the theoretical, in agreement with that found by Hibbert in the case of trimethylstibine, but for triethylstibine the yield was 80–85%.

In view of the ease of oxidation of the trialkylstibines, special precautions were taken to exclude air, both during reactions and in the subsequent separation and manipulation of the products.

Trimethylstibine (Landolt, *Annalen*, 1851, 78, 91) and triethylstibine (Löwig and Schweizer, *ibid.*, 1850, 75, 315, 327) have long been known, but, excepting the preparation of tri-*n*-butylstibine by Morgan and Yarsley (*loc. cit.*), no preparations of higher trialkylstibines have been recorded since 1856, when Berl   (*Annalen*, 1856, 97, 316) prepared a triamylstibine.

The higher trialkylstibines are clear liquids of peculiar odour. Their density falls regularly as the series is ascended, whilst their boiling points rise. When distilled under reduced pressure, the lower members pass over undecomposed, but tri-*n*-hexylstibine is partly decomposed. When cooled to the temperature of liquid air, they crystallise. They are only slightly miscible with water, but at the ordinary temperature they mix in all proportions with alcohol, ether, benzene, and carbon disulphide.

Trialkylstibines combine vigorously with oxygen, which causes an immediate clouding of the originally clear liquid, considerable

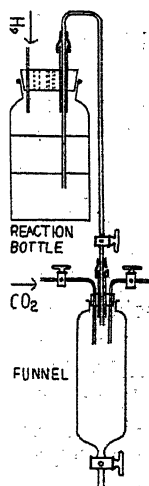
heat being evolved. The avidity for oxygen, however, falls off with increased molecular weight. Stibines readily ignite when warmed in the air, burning with the greyish-green flame characteristic of antimony and evolving clouds of antimonous oxide. When allowed to fall on filter paper, they cause charring and, if in quantity, ignition. Chlorine, bromine, and iodine readily combine with the stibines, dihalides being formed quantitatively. In contradistinction to the phosphines, trialkylstibines combine only lethargically with methyl and other alkyl iodides, and with carbon disulphide they yield no coloured compounds. They reduce mercuric salts in cold aqueous solution, and, on warming, auric and silver salts also, to the metal.

Antimony was determined in the stibines by heating the compound with sodium carbonate in a stream of oxygen in a combustion tube. The contents of the tube were dissolved in 10% hydrochloric acid and antimony trisulphide was precipitated from the boiling solution by the passage of hydrogen sulphide for  $\frac{1}{2}$  hour. An equal volume of hot water was then added to the liquid, and the stream of hydrogen sulphide was continued for 5 minutes. The precipitate was collected on a Gooch crucible, washed, and dried for 2 hours at  $130^{\circ}$  and for 2 hours at  $280\text{--}300^{\circ}$  in carbon dioxide.

#### EXPERIMENTAL.

The apparatus consisted of a wide-necked bottle, of 1 litre capacity, fitted with a rubber stopper carrying a mercury-sealed stirrer, a dropping funnel, a reflux condenser, an inlet tube for hydrogen, and a siphon whereby liquid layers could be withdrawn and separated in absence of air. The exterior limb of the siphon was fitted with a tap and it slid smoothly through a glass jacket fixed in the stopper of a separating funnel (see fig.). Air-tightness was secured by stretching rubber tubing over both the jacket and the limb of the siphon. The other limb of the siphon passed into the reaction bottle by a similar device, which permitted adjustment of the siphon to any desired level. The separating funnel was provided with two tubes with taps to serve either as inlet and outlet, respectively, for carbon dioxide, or for the application of suction.

The Grignard solution was prepared by dropping the freshly prepared alkyl halide, dissolved in 150 c.c. of ether, on 12.1 g. of magnesium turnings immersed in 150 c.c. of ether to which a granule of iodine had been added. Throughout the preparation of this



solution and its interaction with antimony trichloride, pure dry hydrogen was passed over the liquid. The liquid was then cooled to  $0^{\circ}$  and 38.1 g. of freshly redistilled antimony trichloride in 100 c.c. of ether were added drop by drop. After the addition was complete the mixture was warmed for  $\frac{1}{2}$  hour, again cooled to  $0^{\circ}$ , and then treated with ammonium chloride solution. The separating funnel was now filled with pure dry carbon dioxide, and the ethereal layer was transferred from the reaction bottle into the funnel. In this way an unclouded solution was obtained.

In the estimation of the total yield of stibine a standard solution of iodine in ether, or of bromine in carbon tetrachloride, was run into the funnel through the inlet tube until the colour persisted, indicating quantitative conversion into the dihalide.

In cases where the stibine was isolated, the ethereal solution was dried with anhydrous sodium sulphate, the ether distilled off in an atmosphere of carbon dioxide, and the residue fractionally distilled under reduced pressure. A  $2^{\circ}$  fraction containing the stibine was collected in a pycnometer-receiver with a tubular neck and ground-glass stopper. The stibine was thus obtained as a clear liquid.

Triethylstibine was prepared by the addition of the equivalent of antimony trichloride in ether to the Grignard solution prepared from 55 g. of ethyl bromide. The total yield of stibine in the ethereal solution was 80–85%.

*Tri-n-propylstibine*, obtained by the addition of antimony trichloride to magnesium *n*-propyl bromide prepared from 62 g. of the alkyl bromide, has b. p.  $100^{\circ}/25$  mm.,  $113^{\circ}/39$  mm.;  $d_4^{25}$  1.241 (Found: C, 43.2; H, 8.5; Sb, 48.1.  $C_9H_{21}Sb$  requires C, 43.1; H, 8.4; Sb, 48.5%). The total yield of stibine was 60–70%, and the yield of purified material 11 g. The stibine possesses a penetrating, alliaceous odour.

The residue after removal of ether in the case of the interaction between antimony trichloride and magnesium *isopropyl* bromide, on being heated under reduced pressure, continuously emitted gaseous decomposition products. This result is comparable with that obtained in the interaction between various phosphorus chlorides and the Grignard reagent of *isopropyl* bromide (Davies, Pearse, and Jones, J., 1929, 1268).

From the products of the interaction between magnesium *n*-butyl bromide (from 69 g. of *n*-butyl bromide) and its equivalent of antimony trichloride, a first fraction containing *n*-octane was obtained. From this, 5 g. of the purified hydrocarbon, b. p.  $125^{\circ}/760$  mm., were isolated. The distillation was continued under reduced pressure, whereupon there were obtained 11 g. of *tri-n-butylstibine*,

b. p.  $131^{\circ}/12$  mm.;  $d_4^{25}$  1.191 (Found: C, 48.8; H, 9.9; Sb, 40.5.  $C_{12}H_{27}Sb$  requires C, 49.2; H, 9.3; Sb, 41.5%).

*Triisobutylstibine*, b. p.  $135^{\circ}/31$  mm.,  $d_4^{25}$  1.323 (Found: Sb, 41.8.  $C_{12}H_{27}Sb$  requires Sb, 41.5%), was prepared (yield, 11 g.) by the interaction between the antimony halide and magnesium *isobutyl* bromide made from 69 g. of the alkyl bromide. The first runnings furnished 6 g. of  $\beta$ -dimethylhexane, b. p.  $109^{\circ}/760$  mm. The butylstibines possess a mixed alliaceous-butylic odour. The *isobutylstibine* is distinctly yellow.

The preparation of *tri-n-amylstibine* was effected by adding antimony trichloride to the Grignard reagent obtained from 76 g. of *n*-amyl bromide; yield, 15 g., b. p.  $168^{\circ}/16$  mm.,  $d_4^{25}$  1.136 (Found: C, 53.8; H, 9.3; Sb, 37.2.  $C_{15}H_{33}Sb$  requires C, 53.7; H, 9.9; Sb, 36.3%). In the preparation of this stibine there were obtained 8 g. of *n*-decane, b. p.  $88^{\circ}/50$  mm. (Krafft, *Ber.*, 1882, 15, 1695, gives b. p.  $90^{\circ}/50$  mm.).

*Tri-dl- $\beta$ -methylbutylstibine*, obtained from the Grignard reagent made from 76 g. of *dl*- $\beta$ -methylbutyl bromide (yield, 10 g. of purified product), has b. p.  $150^{\circ}/14$  mm.;  $d_4^{25}$  1.242 (Found: Sb, 36.5.  $C_{15}H_{33}Sb$  requires Sb, 36.3%). The synthetic action of the magnesium gave 6 g. of  $\gamma$ -dimethyloctane, b. p.  $159^{\circ}/760$  mm.

The interaction between equivalents of antimony trichloride and magnesium *isoamyl* bromide yielded 10 g. of *triisoamylstibine* (*tri- $\gamma$ -methylbutylstibine*), b. p.  $149^{\circ}/14$  mm.;  $d_4^{25}$  1.227 (Found: Sb, 36.2.  $C_{15}H_{33}Sb$  requires Sb, 36.3%). There were obtained 10 g. of  $\beta$ - $\gamma$ -dimethyloctane, b. p.  $159^{\circ}/760$  mm. When distilled in a stream of carbon dioxide under *atmospheric pressure*, the stibine passed over with considerable decomposition at about  $260^{\circ}$ . All the amyl stibines have a preponderatingly amylic smell. *n*-Amylstibine is colourless, but  $\beta$ - and  $\gamma$ -methylbutylstibines are both yellowish.

*Tri-n-hexylstibine*, prepared (yield 10 g.) from the Grignard reagent made from 83 g. of *n*-hexyl bromide, boils at  $190^{\circ}/10$  mm. with partial decomposition and liberation of antimony. The distillate had  $d_4^{25}$  ca. 1.15. For the purpose of analysis the separated antimony was allowed to settle out of the liquid (Found: Sb, 31.2.  $C_{18}H_{39}Sb$  requires Sb, 32.3%). The smell resembles that of *n*-hexyl alcohol. In this preparation 12 g. of *n*-dodecane, b. p.  $95^{\circ}/12$  mm. (Krafft, *loc. cit.*, gives b. p.  $98^{\circ}/15$  mm.), were obtained.

Investigation of derivatives of the trialkylstibines is being pursued.

## LXIV.—*Syntheses by Means of Magnesium Amyl Halides.*

By WALTER CULE DAVIES, ROBERT SINCLAIR DIXON, and  
WILLIAM JACOB JONES.

ALTHOUGH the magnesium derivatives of *iso*amyl halides have been extensively employed in synthesis, the use of Grignard reagents containing the *n*-amyl radical and, particularly, the  $\beta$ -methylbutyl radical has been rare. Those of the former type have been used by Henry and de Wael (*Rec. trav. chim.*, 1909, **28**, 446), by Pexters (*Bull. Acad. roy. Belg.*, 1906, 796), by Grüttner and Krause (*Ber.*, 1916, **49**, 2666), by Davies, Pearse, and Jones (*J.*, 1929, 1265), and by Dyke, Davies, and Jones (preceding paper); and the Grignard reagent of *dl*- $\beta$ -methylbutyl bromide was used for the first time by Davies, Pearse, and Jones, and later by Dyke, Davies, and Jones, whilst Klages and Sautter (*Ber.*, 1904, **37**, 653) used that prepared from optically active amyl iodide.

The products of the reactions of certain aldehydes and ketones with magnesium *n*-amyl and *dl*- $\beta$ -methylbutyl bromides are now described. In these preparations several types of reaction were encountered, although the conditions were so chosen that the addition reaction yielding carbinol should predominate.

In all cases the decanes were produced as by-products. Under the conditions existing in the present experiments the extent of this synthetic action of metallic magnesium on the amyl bromides was such as to yield about 24 c.c. of decane per 24.3 g. of magnesium. The decane was isolated from the fraction, b. p. 70–100°/50 mm., of the product by shaking with concentrated sulphuric acid, washing with water, drying over sodium, and distillation. In this way were obtained *n*-decane, b. p. 169°/760 mm., and *dl*- $\gamma$ -dimethyloctane, b. p. 79°/50 mm., 159°/760 mm.;  $d_{20}^{25}$  0.7307;  $n_D^{20}$  1.4106;  $[R_L]_D$  48.33 (Calc., 48.38) (Found: C, 84.6; H, 15.3. Calc. for  $C_{10}H_{22}$ : C, 84.5; H, 15.5%) (compare Dupont, *Ann. Chim.*, 1913, **30**, 516).

Enolisation of the reacting ketone by the Grignard compound occurred extensively between acetophenone and magnesium *dl*- $\beta$ -methylbutyl bromide. For instance, purified acetophenone in 52% yield was recovered from the product of reaction, with only 14% yield of the purified tertiary alcohol. In striking contrast thereto was the behaviour of magnesium *n*-amyl bromide with acetophenone, where a 30% yield of purified alcohol was obtained, but no acetophenone was recovered. These results are consonant with the views of Conant and Blatt (*J. Amer. Chem. Soc.*, 1929, **51**, 1236) that the



occurrence of subsidiary reactions, such as enolisation, can be correlated with branching of the alkyl groups involved.

In no case in the present work was reduction met with, but condensation appeared to have occurred in the interaction between methyl *n*-nonyl ketone and magnesium *dl*- $\beta$ -methylbutyl bromide, since an appreciable amount of a substance having a higher b. p. than the carbinol was obtained.

In several cases, details of which are given in the experimental portion, the yield of carbinol was low owing to loss of the elements of water and formation of unsaturated hydrocarbon during the reaction and isolation; and in every case the dehydration was readily effected even on treatment with mild agents.

The preparation of esters of the amylcarbinols, particularly those which contain other higher radicals, is often attended by difficulties. For instance, the acetic ester of *phenylmethyl*-( $\beta$ -methylbutyl)-carbinol was obtained in poor yield, but on being distilled even under reduced pressure it continuously decomposed. Again, in an attempt to prepare the bromide of this carbinol,  $\beta$ -phenyl- $\delta$ -methyl- $\Delta^8$ -hexylene was obtained in good yield. In a similar attempt with *phenyl*-( $\beta$ -methylbutyl)carbinol, the bromide obtained readily parted with hydrogen bromide, yielding *dl*- $\alpha$ -phenyl- $\gamma$ -methyl- $\Delta^4$ -amylene (dibromo-compound, m. p. about 75°), the optically active form of which has been described by Klages and Sautter (*loc. cit.*). In a preparation of the oxalic ester of phenyl-*n*-amylcarbinol, by heating the latter with the anhydrous acid, a considerable amount of unsaturated hydrocarbon was formed, and on distillation the residual oxalate broke down.

The amylcarbinols prepared in the present investigation gave methane with an amyl-ethereal solution of magnesium methyl iodide.

#### EXPERIMENTAL.

*Preparation of Carbinols.*—The aldehyde or ketone in ethereal solution was dropped into the filtered Grignard solution, which was kept at 10°. Equivalent weights of the reactants were used. After the addition was complete the mixture was gently boiled for  $\frac{1}{2}$  hour, poured on ice, and treated with sufficient mineral acid to dissolve the precipitated magnesium salts. The ethereal layer was washed with sodium bicarbonate solution, with the addition, where necessary, of sodium bisulphite solution. The dried ethereal solution was fractionally distilled under 50 mm. pressure. The carbinol fraction was redistilled.

*Preparation of Ketones.*—20 C.c. of the secondary alcohol were gradually added with shaking and cooling to 100 c.c. of a saturated solution of potassium dichromate in 20% aqueous sulphuric acid.

The mixture was then mechanically shaken for 5 hours. The resulting ketone was extracted with ether, isolated by fractional distillation, redistilled, and purified by freezing where possible.

All thermometer readings given have been corrected.

*Phenyl-n-amylcarbinol* was prepared by the addition of 106 g. of benzaldehyde in 100 c.c. of ether to a Grignard solution made from 151 g. of *n*-amyl bromide, 24.3 g. of magnesium, and 500 c.c. of ether. The alcoholic fraction distilled at 167–171°/50 mm., and on redistillation yielded 64 g. of pure alcohol, a thick liquid, b. p. 170°/50 mm.;  $d_4^{25}$  0.9477;  $n_D^{25}$  1.5042;  $[R_L]_D^{25}$  55.65 (Calc. for  $C_{12}H_{18}O$ , 3 $\bar{5}$ , 55.54);  $n_F^{25} - n_C^{25}$  0.0136 (Calc., 0.0122) (Found: C, 81.1; H, 9.9.  $C_{12}H_{18}O$  requires C, 80.9; H, 10.1%). Phenyl *n*-amyl ketone, m. p. 27° (semicarbazone, m. p. 132°) (compare Schroeter, *Ber.*, 1907, 40, 1603), was obtained on oxidation of the alcohol.

From the products of the interaction between anisaldehyde and magnesium *n*-amyl bromide there was obtained a considerable amount of anisaldehyde, identified by b. p., 164°/50 mm. (literature gives 166°/50 mm.), and by conversion into anisic acid, m. p. 184°. The first fractional distillation of the product also gave *p*-methoxyphenyl-*n*-amylcarbinol, b. p. 207–210°/50 mm. On being redistilled at low pressures this carbinol partly decomposed with elimination of water, a behaviour similar to that observed by Stedman and Stedman (*J.*, 1929, 614) in the case of the corresponding methyl carbinol. On this account the carbinol distillate was saturated with hydrogen chloride and then boiled with excess of pyridine, whereby, after treatment with water, there was obtained  $\alpha$ -*p*-methoxyphenyl- $\Delta^2$ -hexylene, b. p. 187–188°/50 mm.;  $d_4^{25}$  0.9594;  $n_D^{25}$  1.5356;  $[R_L]_D^{25}$  61.77 (Calc. for  $C_{13}H_{18}O$ , 4 $\bar{4}$ , 59.81);  $n_F^{25} - n_C^{25}$  0.0213 (Calc., 0.0134) (Found: C, 81.4; H, 9.7.  $C_{13}H_{18}O$  requires C, 82.0; H, 9.5%). This compound readily adds on bromine.

*Methylethyl-n-amylcarbinol* was prepared by adding 72 g. of methyl ethyl ketone in 75 c.c. of ether to the Grignard reagent formed by 151 g. of *n*-amyl bromide, 24.3 g. of magnesium, and 500 c.c. of ether. The alcoholic fraction after several redistillations yielded 35 g. of the purified carbinol, b. p. 97.5°/50 mm.;  $d_4^{25}$  0.8108;  $n_D^{25}$  1.4257;  $[R_L]_D^{25}$  45.52 (Calc., 45.29);  $n_F^{25} - n_C^{25}$  0.0077 (Calc., 0.0074) (Found: C, 75.5; H, 13.8.  $C_9H_{20}O$  requires C, 74.9; H, 14.0%). The carbinol is a mobile liquid, possessing a characteristic, slightly peppermint-like, smell.

*Methyl-n-amyl-n-nonylcarbinol* was obtained from the product of the interaction between 170 g. of methyl *n*-nonyl ketone, dissolved in 100 c.c. of ether, and magnesium *n*-amyl bromide prepared from the equivalent of the amyl bromide. The ketone was obtained by washing oil of rue successively with 20% sulphuric acid, 5% sodium

carbonate, and 5% sodium hydroxide solutions, and fractionally distilling it under reduced pressure, and was finally purified by repeated freezing (Sanderson and Jones, *J. Soc. Chem. Ind.*, 1923, 42, 1). The interaction between the ketone and the Grignard reagent was not vigorous, and, for that reason, the mixture was kept for 12 hours. The usual separation of the magnesium salt-complex was not observed in this case, but the treatment with crushed ice and mineral acid was continued as in the other preparations. The ether having been expelled, the product was repeatedly fractionally distilled under 50 mm. pressure, whereby there were obtained the following main fractions: (1) up to 115°, decane, which on treatment with concentrated sulphuric acid gave 20 c.c. of the hydrocarbon; (2) 143—147°, methyl *n*-nonyl ketone, 50 c.c., identified by its semicarbazone, m. p. 123°; (3) 199—200°, methyl-*n*-amyl-*n*-nonylcarbinol, 80 c.c.;  $d_4^{25}$  0.8316,  $n_D^{25}$  1.4446,  $[R_L]_D$  77.50 (Calc., 77.61),  $n_F^{25} - n_C^{25}$  0.0079 (Calc., 0.0079) (Found: C, 79.7; H, 14.2.  $C_{16}H_{34}O$  requires C, 79.3; H, 14.2%). The large amount of recovered ketone suggests enolisation. It is noteworthy that the only previous application of the Grignard reagent to this ketone was in the preparation of dimethyl-*n*-nonylcarbinol (Houben, *Ber.*, 1902, 35, 3591).

*Phenylmethyl-n-amylcarbinol* has b. p. 169°/50 mm.;  $d_4^{25}$  0.9389;  $n_D^{25}$  1.5028;  $[R_L]_D$  60.47 (Calc. for  $C_{13}H_{20}O, 3$ , 60.16);  $n_F^{25} - n_C^{25}$  0.0131 (Calc., 0.0119) (Found: C, 80.5; H, 9.8.  $C_{13}H_{20}O$  requires C, 81.2; H, 10.5%). It was prepared by the interaction of 120 g. of acetophenone with the magnesium *n*-amyl bromide made from 151 g. of the bromide and 24.3 g. of magnesium. The crude carbinol fraction contained unsaturated hydrocarbon, from which the carbinol was purified by redistillation; yield, 58 g.

Methyl  $\beta$ -methylbutyl ketone has been prepared by Kohler (*Amer. Chem. J.*, 1907, 38, 527) from ethylideneacetone and magnesium ethyl bromide, and by Clarke (*J. Amer. Chem. Soc.*, 1908, 30, 1150) by the hydrolysis of ethyl *sec*-butylacetoacetate. We have now prepared it by treatment of the carbinol fraction, 68—73°/50 mm., obtained from the interaction between acetaldehyde and magnesium *dl*- $\beta$ -methylbutyl bromide, with a saturated solution of potassium dichromate in 20% sulphuric acid. The ketone was purified through its semicarbazone, 62 c.c. of the crude material being mechanically stirred on the water-bath for 2 hours with 38 g. of semicarbazide hydrochloride, 47 g. of sodium acetate trihydrate, 12 c.c. of ethyl alcohol, and 140 c.c. of water. The solid semicarbazone was recrystallised from aqueous alcohol, and gave 27 g. of pure product.

*Methyl  $\beta$ -methylbutyl ketone semicarbazone*, m. p. 120—121°

(Found: N, 24.2.  $C_8H_{17}ON_3$  requires N, 24.5%), was converted by 1 hour's boiling with 15% hydrochloric acid into the ketone, b. p.  $68^\circ/50$  mm.,  $69.5^\circ/57$  mm.;  $d_4^{25}$  0.8085;  $n_D^{25}$  1.4050;  $[R_L]_D$  34.56 (Calc., 34.54);  $n_F^{25} - n_C^{25}$  0.0073 (Calc., 0.0074) (Found: C, 74.0; H, 12.5. Calc. for  $C_7H_{14}O$ : C, 73.7; H, 12.4%).

Klages and Sautter (*loc. cit.*) state that the product of interaction between benzaldehyde and the magnesium derivative of active amyl iodide consists chiefly of active hexenylbenzene, together with some of the carbinol, which they did not isolate. In the present experiments, however, no difficulty was experienced in isolating the inactive carbinol in pure condition and fair yield. Moreover, no elimination of water from the carbinol during reduced-pressure distillation was noticed (contrast Klages and Sautter, *loc. cit.*). *Phenyl-( $\beta$ -methylbutyl)carbinol* (yield, 40 g.), obtained by the addition of 106 g. of benzaldehyde to magnesium *dl*- $\beta$ -methylbutyl bromide prepared from 151 g. of the *dl*-amyl bromide, has b. p.  $163^\circ/50$  mm.;  $d_4^{25}$  0.9523;  $n_D^{25}$  1.5059;  $[R_L]_D$  55.51 (Calc. for  $C_{12}H_{18}O, 3$ ], 55.54);  $n_F^{25} - n_C^{25}$  0.0143 (Calc., 0.0123) (Found: C, 81.0; H, 10.0; OH, 8.3.  $C_{12}H_{18}O$  requires C, 80.9; H, 10.1; OH, 9.5%). On dehydration the carbinol yielded unsaturated hydrocarbon. *Phenyl  $\beta$ -methylbutyl ketone* (Found: C, 81.4; H, 9.0.  $C_{12}H_{16}O$  requires C, 81.8; H, 9.1%) boils at  $163^\circ/50$  mm.;  $d_4^{25}$  0.9640;  $n_D^{25}$  1.5093;  $[R_L]_D$  54.49 (Calc. for  $C_{12}H_{16}O, 3$ ], 54.03);  $n_F^{25} - n_C^{25}$  0.0156 (Calc., 0.0127). The *semicarbazone* (Found: N, 18.3.  $C_{13}H_{19}ON_3$  requires N, 18.0%), m. p.  $160^\circ$ , separates as rods from alcohol.

In an attempt to prepare *p*-methoxyphenyl  $\beta$ -methylbutyl ketone, by oxidising the product obtained from the interaction of magnesium *dl*- $\beta$ -methylbutyl bromide with anisaldehyde, considerable amounts of anisaldehyde and anisic acid were obtained, but no ketone.

*Methylethyl-( $\beta$ -methylbutyl)carbinol*, b. p.  $95-97^\circ/50$  mm.;  $d_4^{25}$  0.8177;  $n_D^{25}$  1.4251;  $[R_L]_D$  45.10 (Calc., 45.29);  $n_F^{25} - n_C^{25}$  0.0076 (Calc., 0.0075) (Found: C, 74.6; H, 13.9.  $C_9H_{20}O$  requires C, 74.9; H, 14.0%), results (in 25 g. yield) from the interaction of 72 g. of methyl ethyl ketone in 100 c.c. of ether with magnesium *dl*- $\beta$ -methylbutyl bromide made from 151 g. of the bromide and 24.3 g. of magnesium. The smell of the carbinol resembles that of the corresponding *n*-amyl carbinol, but is more penetrating.

*Methyl-( $\beta$ -methylbutyl)-*n*-nonylcarbinol* was prepared by treating 170 g. of methyl *n*-nonyl ketone in 100 c.c. of ether with magnesium *dl*- $\beta$ -methylbutyl bromide prepared from the equivalent of the alkyl bromide, and keeping the reaction mixture for 12 hours. Here also, as in the preparation of methyl-*n*-amyl-*n*-nonylcarbinol,

there was no separation of the magnesium salt-complex. After treatment with mineral acid and removal of ether, the resulting oil was repeatedly fractionally distilled at 50 mm. Methyl *n*-nonyl ketone (90 c.c., identified by b. p. and semicarbazone) was recovered. The carbinol fraction (32 c.c.; b. p. 194–202°) was twice redistilled, but yet was not satisfactorily purified. The fraction of b. p. 198–200°/50 mm. (Found: C, 77.4; H, 13.8.  $C_{16}H_{34}O$  requires C, 79.3; H, 14.2%) has  $d_4^{25}$  0.8301;  $n_D^{25}$  1.4438;  $[R_L]_D$  77.50 (Calc., 77.61). The residue, 27 c.c., left after distillation of the carbinol fraction, on being redistilled yielded 11 c.c. of liquid, b. p. 255–265°/50 mm. This substance appears to be  $CH_3 \cdot C(C_5H_{11})(C_9H_{19}) \cdot O \cdot C_5H_{11}$  (Found: C, 81.9; H, 13.7; *M*, 295.  $C_{21}H_{44}O$  requires C, 80.7; H, 14.2%; *M*, 312);  $d_4^{25}$  0.8433;  $n_D^{25}$  1.4582;  $[R_L]_D$  103.5 (Calc., 100.8).

Enolisation was encountered in the interaction between equivalents of acetophenone (120 g.) and magnesium *dl*-β-methylbutyl bromide. Fractionation of the crude product gave (1), b. p. 105–140°/50 mm., 72 g., which on redistillation yielded 62 g. of acetophenone, b. p. 115°/50 mm. (Found: C, 80.1; H, 7.0. Calc.: C, 80.0; H, 6.7%), and (2), b. p. 140–170°/50 mm., 48 g., which on redistillation yielded 27 g. of *phenylmethyl*-(β-methylbutyl)carbinol, b. p. 163.5°/50 mm.;  $d_4^{25}$  0.9388;  $n_D^{25}$  1.5027;  $[R_L]_D$  60.47 (Calc. for  $C_{13}H_{20}O, 3\frac{1}{2}$ , 60.16);  $n_D^{25} - n_D^{20}$  0.0137 (Calc., 0.0119) (Found: C, 81.1; H, 10.2; OH, 8.6.  $C_{13}H_{20}O$  requires C, 81.2; H, 10.5; OH, 8.8%). On dehydration, the carbinol yielded β-phenyl-δ-methyl-Δ<sup>β</sup>-hexylene, b. p. 142°/50 mm.;  $d_4^{25}$  0.8839;  $n_D^{25}$  1.5117;  $[R_L]_D$  59.10 (Calc. for  $C_{13}H_{18}, 4\frac{1}{2}$ , 58.16);  $n_D^{25} - n_D^{20}$  0.0167 (Calc., 0.0132) (Found: C, 89.4; H, 10.3.  $C_{13}H_{18}$  requires C, 89.6; H, 10.4%).

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## LXV.—The Reduction of Triphenylhalogenomethanes.

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THE utility of certain heavy metals for the reduction of triphenylhalogenomethanes has been demonstrated in the classical investigations of Gomberg (*Ber.*, 1900, **33**, 310) on the preparation of the free radical, triphenylmethyl, and in subsequent work (*Chem. Reviews*, 1924, **1**, 99) on various triarylmethyls. In the case of triphenylchloromethane in benzene solution it was shown that the halogen is quantitatively removed by zinc, and that the reduction is also effected by mercury and silver. Copper, in the form of

Naturkupfer-C, has been employed by Schlenk (*Annalen*, 1909, **372**, 17) for the same purpose, but in this instance the application of heat is usually necessary for the completion of the reaction. The investigation of the action of magnesium on triphenylchloromethane in ethereal solution by Schmidlin (*Ber.*, 1906, **39**, 4183) led to the elaboration of a method for the preparation of triphenylmethyl through the interaction of magnesium triphenylmethyl chloride with triphenylchloromethane (*Ber.*, 1908, **41**, 423).

More recently, Kraus and Kawamura (*J. Amer. Chem. Soc.*, 1923, **45**, 2756) have studied the action of sodium and potassium upon triphenylchloromethane in liquid ammonia, and have found that the primary reduction is followed by the combination of free radical with alkali metal to give the corresponding triphenylmethide. The colour which is produced when liquid ammonia solutions of triphenylmethyl are treated with metallic calcium led these authors to infer the existence of calcium triphenylmethide.

It was observed by Schlenk and Marcus (*Ber.*, 1914, **47**, 1678) that triphenylmethyl in ethereal solution on treatment with sodium is converted into *p*-benzhydryltetraphenylmethane. Sodium triphenylmethide, however, is obtained when an ethereal solution of triphenylchloromethane is treated with sodium amalgam. Grosse (*Ber.*, 1926, **59**, 2652) has shown that lithium, rubidium, and caesium triphenylmethides may be obtained by agitating the aryl chloride in ethereal solution with the corresponding amalgam.

In view of the comparative ease with which triphenyl-chloro- and -bromo-methanes undergo reduction by the heavy metals, it is of interest to note that Blicke (*J. Amer. Chem. Soc.*, 1924, **46**, 1515) was not able to reduce triphenylfluoromethane by means of silver.

No systematic survey of the action of other metals on triphenyl-chloro- and -bromo-methanes has hitherto been undertaken, and we have accordingly carried out a preliminary investigation of the action of a series of representative elements.

The influence of the solvent upon the reaction between triphenyl-halogenomethanes and metals is very marked, and is to be referred primarily to two factors. The first is largely a physical influence, and in view of the heterogeneity of the reaction system, it follows that in those cases where an "active" metallic surface is maintained, as a result of the solution or disintegration of the metallic halide formed on the surface of the metal, an increase will be evident in the rate and extent of reduction. The second is the purely chemical influence, in which the constitutional effect of the solvent is evident in modifying the molecular state of the aryl halide in solution, and in further determining the character of the interfacial phenomena which obtain at the metal-solution interface. These factors are

brought into special prominence in the present investigation by a comparison of the behaviour of acetone and of benzene with that of *n*-hexane. Reduction of triphenylchloromethane in *n*-hexane is effected by only few metals; even with mercury and silver, reaction proceeds much more slowly than in benzene.

Cadmium, thallium, lead, tin, arsenic, antimony, bismuth, selenium, tellurium, and iron were found to react with triphenylchloro- and -bromo-methanes in benzene, toluene, and ethereal solution. The rate of reaction differs considerably in the various cases, the most reactive metal being iron and the least reactive lead. The reduction of triphenylchloromethane by cadmium takes place considerably more slowly than by zinc. Triphenylchloromethane in benzene, toluene, bromobenzene, hexane, or ether is not attacked by cobalt or nickel, and only to a slight extent by manganese and chromium.

In several cases the direct reduction is followed by secondary reactions, which may involve (a) combination of metallic halide with unchanged aryl halide, (b) interaction of the liberated free radical with the metallic halide, (c) combination of the free radical with unchanged element, and (d) interaction of the metallic halide with the solvent. Triphenylbromomethane is rapidly reduced by zinc and tin, the initial reaction being followed by the combination of the metallic bromide with unchanged aryl bromide to give highly coloured addition compounds. The addition of finely divided iron to a benzene solution of triphenylchloromethane immediately produces a yellow coloration, which rapidly increases in intensity until the final colour is greenish-yellow. This solution does not contain free triphenylmethyl, and no triphenylmethyl peroxide is obtained by the prolonged action of oxygen. The evidence would seem to indicate the existence in solution of a stable triphenylmethyl-ferrous chloride complex.

Aluminium, as pure powder, appears to have no action on benzene solutions of triphenylchloromethane at the ordinary temperature, but reaction occurs fairly rapidly with the turnings of the commercial metal. In this reaction, the primary reduction is followed by the formation of an addition compound with aluminium chloride. When, however, the reaction is carried out in acetone, interaction occurs between the aluminium chloride and the solvent, and in some cases the solution sets to a gel in the course of a few days.

The behaviour of cobalt, manganese, and chromium towards triphenylchloromethane in acetone is remarkable, inasmuch as rapid and complete reduction to triphenylmethyl takes place. This reactivity is in direct contrast to the behaviour of these metals towards solutions of the substance in benzene, toluene, bromobenzene,

ether, and hexane. In this connexion, it may be mentioned that tritolylchloromethane in acetone solution has been shown by Norris (*Amer. Chem. J.*, 1907, **38**, 627) to conduct the electric current. In like manner, we find that triphenylchloromethane exhibits a marked conductivity in this solvent, but that in the fused state it is not a conductor.

In several cases anomalous results were obtained with acetone solutions of triphenyl-chloro- and -bromo-methanes, and we have ascertained that this is due to a reaction other than that between metal and the aryl halide. Even at the ordinary temperature, triphenylbromomethane interacts slowly with the enolic form of acetone, the solution assuming a dark brownish colour in the course of a few days. This reaction will be the subject of a further communication.

Both calcium and nickel are entirely non-reactive towards the triphenylhalogenomethanes in all the solvents examined (except possibly acetone), and magnesium is also extremely lethargic except with ethereal solutions. In the latter case, magnesium triphenylmethyl chloride is formed on prolonged agitation at the ordinary temperature and in the absence of external catalyst.

#### EXPERIMENTAL.

In order to avoid the complicating influences of atmospheric oxidation, all the experiments were conducted in the entire absence of air. In general, therefore, the reactions were carried out at the ordinary temperature in sealed tubes. Excess of the element was placed in a suitably constricted tube, and after all the air had been displaced by pure dry carbon dioxide, the tube was almost completely filled with a standard solution of the triphenylhalogenomethane. A small amount of the pure solvent was added in order to remove the film of solution from the constriction, and the tube was then sealed under carbon dioxide. The tubes, together with standard comparison tubes containing silver or mercury, were placed in a shaking machine, and their contents agitated in the dark for specified periods and then examined. Triphenylmethyl was recognised by its characteristic colour, and by its conversion into triphenylmethyl peroxide under the influence of oxygen or into diphenylbisdiphenylene-ethane on irradiation.

In many cases it was necessary to conduct the experiments on a larger scale, and for this purpose the triphenyl-chloro- or -bromo-methane solution and the finely powdered element were placed in a flask, which could be charged with carbon dioxide. After the contents had been agitated for the stipulated period, the solution was drawn under carbon dioxide through a suitable filter into a



partly evacuated vessel, where its nature was examined. The following experiment is representative of the methods employed.

Triphenylchloromethane (5 g.) in acetone (50 c.c.) was agitated under carbon dioxide with excess of metallic cobalt for 3 hours. The resulting greenish-blue solution was filtered in an atmosphere of carbon dioxide, and the filtrate divided into two parts. Air was passed through the first portion, whereupon the solution assumed a blue colour with simultaneous precipitation of finely crystalline triphenylmethyl peroxide, m. p.  $183^{\circ}$ ; yield 60%. The second portion of the filtrate was exposed in a sealed tube to direct sunlight. Photochemical decomposition proceeded more rapidly than with the ordinary yellow solutions of triphenylmethyl in benzene (Bowden and Jones, J., 1928, 1150); the solution became blue, and diphenyl-bisdiphenylene-ethane, m. p. (in a vacuum)  $248-250^{\circ}$ , was precipitated. The presence of cobaltous chloride in the above solutions was demonstrated by the usual tests.

*Interaction of Triphenylbromomethane with Acetone.*—Pure recrystallised triphenylbromomethane (10 g.) was dissolved in dry, acid-free acetone (245 c.c.) in a flask which was then sealed and kept in the dark at the ordinary temperature. The freshly prepared solution was colourless, but after standing for 3 or 4 days, it was brownish-yellow, which changed to a deep dark brown after 12 weeks. At the end of this period the solution was divided into two portions, solution A (205 c.c.) and solution B (40 c.c.), which were examined in the following manner.

*Solution A.* This portion was subjected to careful fractionation through a long Vigreux column, the receiving flask being cooled in a freezing mixture in order to ensure the retention of low-boiling products. Examination of the first portions of the distillate showed the absence of hydrogen bromide and of  $\beta$ -bromopropylene, b. p.  $48^{\circ}$ . After removal of the bulk of acetone, the residual liquid (40 c.c.) was placed in a tightly-stoppered flask and cooled in ice. After some hours, impure triphenylcarbinol (1.2 g.) was deposited. The filtrate was agitated under nitrogen with excess of metallic silver for several hours, after which the solution was filtered in an atmosphere of nitrogen. Dry air was passed through the filtrate in order to effect the complete oxidation of triphenylmethyl formed by the reduction of unchanged triphenylbromomethane. In this manner, crude triphenylmethyl peroxide (0.22 g.), m. p.  $175-178^{\circ}$ , was obtained.

*Solution B.* This solution was agitated under nitrogen with excess of silver for several hours, filtered in a stream of nitrogen, and the clear filtrate oxidised by means of a current of air. The precipitated peroxide (0.18 g.) was practically white; m. p.  $182-183^{\circ}$ .

Preliminary experiments showed that the yield of peroxide obtainable from freshly prepared solutions of triphenylbromomethane was 65%. On this basis, the above results show that 79.2% of the triphenylbromomethane interacted with acetone at the ordinary temperature.

*Addition Compounds of Triphenylbromomethane.*—The following addition compounds of triphenylbromomethane with metallic bromides were prepared during the course of the investigation.

*With aluminium bromide.* Anhydrous aluminium bromide, dissolved in carbon disulphide, was added to a slight excess of triphenylbromomethane in benzene solution. The dark red oil, which separated immediately, was washed rapidly with benzene, and finally with carbon disulphide. After being preserved for some hours in a vacuum, it crystallised in cubes, m. p. 120—123° [Found: C, 37.9; H, 2.6; Br, 53.5; Al, 4.4.  $(C_6H_5)_3CBr, AlBr_3$  requires C, 38.6; H, 2.5; Br, 54.2; Al, 4.6%].

*With zinc bromide.* This compound was precipitated by mixing benzene solutions of triphenylbromomethane and zinc bromide. The dark red oil could not be induced to crystallise [Found: C, 41.0; H, 3.1; Br, 42.9; Zn, 11.6.  $(C_6H_5)_3CBr, ZnBr_2$  requires C, 41.6; H, 2.8; Br, 43.7; Zn, 11.9%].

*With stannic bromide.* This compound, prepared as in the preceding case, was obtained in the crystalline condition, m. p. 171°, after treatment with hexane [Found: C, 29.1; H, 2.1; Br, 52.3; Sn, 15.1.  $(C_6H_5)_3CBr, SnBr_4$  requires C, 29.9; H, 2.0; Br, 52.5; Sn, 15.6%].

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## LXVI.—*The Passivity of Metals. Part IV. The Influence of Acids in Passivity and Corrosion.*

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In general, acids dispel passivity and accelerate the corrosion of iron. Occasionally, however, passivity is obtained with acid media, and it has been argued that in such cases the passivity cannot be due to oxide films, which would—it is urged—be dissolved by the acid. One important case, the action of concentrated nitric acid, has been elucidated by Hedges (J., 1928, 969), who finds that, under the conditions where passivity arises, nitric acid has no appreciable solvent power for ferric oxide, which is therefore regarded as the cause of the passivity. Lately Benedicks and Sederholm (*Z. physikal. Chem.*, 1928, 138, 123) have advanced direct evidence that the passivity produced by nitric acid diluted with

alcohol and water is also due to a protective film; here it is considered that the film is ferrous oxide in the inner portions, and hydrated ferric oxide ( $\text{FeO}\cdot\text{OH}$ ) in the outer portions. This seems much more likely than the contention of Fujihara (*Ind. Eng. Chem.*, 1926, 18, 62), that the passivity produced by alcoholic nitric acid is due solely to ferrous hydroxide, which is supposed to cause passivity by maintaining an alkaline reaction; treatment with nitric acid would scarcely leave an alkaline reaction, whilst in any case ferrous hydroxide is unlikely to escape dissolution or further oxidation in such a medium. There seems no reason to doubt that the passivity is due to an oxide film which—at least on the outside—is in the ferric condition.

Two other cases remain to be explained, *viz.*, the passivity produced (1) by immersion in chromic acid and (2) by anodic treatment in dilute sulphuric acid.

*Action of Chromic Acid on Iron.*—There seems to be little information available as to the oxide-solvent powers of chromic acid, or the exact conditions under which it produces passivity. Dunstan, Jowett, and Goulding (J., 1905, 87, 1571) have kept iron bright in chromic acid solution for ten years; but Moody (P., 1903, 19, 158) states that there is a slow dissolution, whilst van Name and Hill (*Amer. J. Sci.*, 1916, 42, 301) have found that mixtures of chromic and sulphuric acids (the latter in excess) cause rapid corrosion. Many samples of "chromic acid" contain sulphuric acid, and it was decided to conduct some new experiments with Kahlbaum's "Chromic Acid, free from Sulphuric Acid." For analyses of the specimens of metal employed, see J., 1929, 93.

It was found that *M*/10-chromic acid did not evolve carbon dioxide from sodium or ammonium carbonate, and failed to dissolve freshly precipitated ferric hydroxide, even on standing over it for several days. The solution had no effect on the colours of heat-tinted iron, even after 24 hours, although *M*/10-sulphuric acid produces an appreciable alteration in a few seconds. Apparently, therefore, chromic acid does not dissolve flaky ferric oxide.

Strips of iron H 28, 2 cm. wide, were abraded with French emery No. 1, degreased, and immersed vertically to a depth of 3.5 cm. in 90 c.c. of chromic acid-sulphuric acid mixtures for 6 hours at 14.0°. The mixtures acted rapidly on the metal, producing ferric and chromic sulphates, and the layer of largely exhausted solution, which had an enhanced specific gravity, sank rapidly down the vertical surface, fresh solution being drawn in at the top. Owing to the partial exhaustion, the numbers given in Table I do not indicate the velocity coefficient, but they show very clearly that (a) at constant concentration of sulphuric acid, chromic acid increases the

attack, evidently acting as a depolariser, since no hydrogen appears when it is present, and (b) at constant concentration of chromic acid, sulphuric acid increases the attack; in the absence of sulphuric acid, chromic acid produced no visible change, but the small loss of weight measured was confirmed by experiments with chromic acid from another source.

TABLE I.

	H <sub>2</sub> SO <sub>4</sub> (mol./l.).	CrO <sub>3</sub> (mol./l.).	Loss of weight, mg.	Mean, mg.
(a)	0.05	Nil	9.3, 10.2	9.7
	0.05	0.005	25.0, 26.8	25.9
	0.05	0.01	40.9, 44.5	42.7
	0.05	0.02	76.6, 79.2	77.9
	Nil	0.01	0.2, 0.3	0.2
(b)	0.02	0.01	37.6, 38.9	38.2
	0.05	0.01	40.9, 44.5	42.7
	0.09	0.01	54.2, 57.5	55.8

Another series of experiments conducted for 20 hours led to the same conclusions. It was found that immersion in *M*/10-chromic acid for 6 hours rendered the iron passive towards *M*/20-copper nitrate, but not towards copper sulphate, although the latter reagent deposited copper less readily than on the iron merely exposed to air. This was best shown by placing drops of copper sulphate in such a position that only half the drop lay on the area which had been immersed in chromic acid. Copper appeared quickly on the half previously exposed to air, and only slowly on the other half, the line of demarcation being very sharp.

Since chromic acid has powerful oxidising but weak base-dissolving properties, it is easy to understand why it enhances corrosion in the presence of a stronger acid, but produces a protective oxide film when acting alone; the case is completely analogous to that of concentrated nitric acid.

*Passivity produced by Anodic Treatment in Dilute Sulphuric Acid.*—Tronstad (*Z. physikal. Chem.*, 1929, **142**, 272) has proved optically that an oxide film exists on a nickel anode rendered passive in acid solution, but W. J. Müller (*Z. Elektrochem.*, 1928, **34**, 583; *Monatsh.*, 1929, **52**, 463, 474), whilst agreeing that oxide films play an essential part in many types of passivity, considers that iron oxide could not survive in an acid solution, and cannot therefore be the cause of the passivity of an iron anode. This objection has now been examined experimentally.

The fact that sulphuric acid destroys the first-order temper-colours seems to justify the idea that ferric oxide in the form of films is soluble in the acid; the thinning or removal of the films is easily recognisable at *M*/500-concentration after 1 minute's immersion, and becomes very rapid at greater concentrations. *M*/10-

Sulphuric acid, besides rapidly destroying the thin oxide films, also attacks the metal, and the thicker films (above second-order thickness) peel off in flakes, before they are completely destroyed. Now, *when these oxide flakes pass out of electrical contact with the metallic basis, the solvent action practically ceases*; flakes have been preserved in  $M/10$ -acid for long periods without serious change; in one case, they retained their characteristic flake form after standing for 18 days in the acid, although becoming eaten through in places. This suggests that the rapid destruction of the films when in contact with the metal is simply due to the formation, at the various cracks in the film, of the short-circuited cell metal|acid|ferric oxide. The ferric oxide, being the cathode, is rapidly reduced to ferrous oxide, which at once dissolves. Actually, cathodic reduction, conducted with an external source of *E.M.F.*, was employed in earlier work (*Proc. Roy. Soc.*, 1925, *A*, 107, 228) to bring about the uniform thinning of the films.

If this is the true explanation, it should be possible, by using an oxidising agent, to prevent reduction, and thus retard the destruction of the films. A strip of iron, heated at one side so as to give the complete sequence of tints, was partly immersed in a solution containing sulphuric ( $M/100$ ) and chromic acid ( $M/10$ ). After 24 hours, there was not the smallest alteration of any colour. Yet  $M/100$ -sulphuric acid, free from chromic acid, causes appreciable change in 5 seconds, and complete destruction of the earlier colours in 1 minute. Experiments with more concentrated sulphuric acid were complicated by the attack on the metallic basis, but here also the life of the colours was greatly prolonged by the presence of chromic acid.

The rational way to prevent cathodic reduction is to submit the specimen, as a whole, to anodic treatment. A series of experiments was performed in which the anode and cathode were vertical strips 2.0 cm. broad, clamped 3.8 cm. apart, and immersed for a depth of 2.0 cm. The cathode was a plain piece of iron, but the anode, after being ground with French emery No. 1 and degreased, was usually given an appropriate oxidising treatment before the experiment. The liquid was  $M/10$ -sulphuric acid and the *E.M.F.* was 4.0 volts. Except where otherwise stated, the electrodes were connected to the battery *before* introduction into the liquid, so that current commenced to flow from the moment of immersion—a plan previously adopted by Hedges (*J.*, 1926, 2879). The current forced through the cell varied somewhat with the time and pre-treatment, but it always rose to about double its previous value when the iron passed from the passive state into the fully active state. Where the back of the anode was protected by nitrocellulose,

the current was usually about 0.12 amp. (passive) and 0.24 amp. (active).

When the iron anode had been tinted by heating in air on a lead-tin bath, oxygen was evolved from the moment of introduction, and the anode suffered no corrosion and no change of colour. A short interruption of current (a fraction of a second, and sometimes several seconds) did not dispel passivity; in these cases evolution of oxygen recommenced when the circuit was restored, the anode remaining unattacked. But a longer interruption destroyed passivity, and when the circuit was restored, the current jumped to the higher value, the iron began to dissolve, and no further oxygen was produced. With comparatively thick (second-order) films, an interruption of, say, 15 seconds did not destroy the film entirely, but it allowed attack on the iron to commence at certain points, and a series of such interruptions, with intervening periods during which current was allowed to flow, produced complete undermining of the film, which peeled off in characteristic curling flakes; once out of contact with the metal, the oxide film could be kept in the acid for hours without damage. Thinner (first-order) films were completely destroyed by an interruption of a duration which would only cause undermining of the thicker films; the colour vanished, revealing unchanged iron below, and on restoration of the circuit, the iron became etched without any signs of peeling. On the other hand, in experiments when the circuit was restored at the moment when the film had been destroyed at some points, but not everywhere, the thin film peeled off from the parts where it survived; it could then be washed free from acid, and preserved indefinitely.

Although useless for quantitative purposes, this proved a convenient way of preparing oxide films (especially the thicker films) in a state free from secondary hydroxide. The films showed the same behaviour to reagents as those separated by the iodine method, being turned blue by acid ferrocyanide, but not by acid ferricyanide (except, in some cases, at local spots representing inclusions). The film substance is thus ferric oxide with occasional inclusions (metallic iron, or possibly, in some cases, magnetite); the film fragments showed a very feeble response to the magnet, but this has no significance, since ferric oxide can exist in a magnetic form (Welo and Baudisch, *Phil. Mag.*, 1925, 50, 399; 1927, 3, 396).

Unheated specimens simply exposed to air after being ground and degreased showed irregular behaviour when exposed to anodic treatment in *M*/10-sulphuric acid. Occasionally they were active from the moment of immersion; in other cases, after identical treatment, they were passive from the moment of immersion, and after oxygen had passed for a minute, the current could be inter-

rupted for a limited period without loss of passivity. The interruption which could be tolerated without causing activity varied somewhat from one specimen to another, and seemed to depend on the time during which current had been passing, but the following observation appeared to provide the explanation. After the current had been interrupted, small oxygen bubbles continued to be evolved for some seconds, slackening as the supercharge of oxygen became exhausted. If the circuit was restored *before* this evolution of "residual" oxygen ceased, the iron remained passive and a lively production of oxygen set in again as soon as the current began to flow; but if the interruption was prolonged until the slow evolution of "residual" oxygen had completely ceased, the iron became active, and began to dissolve, without oxygen evolution, when the circuit was restored; evidently a considerable supercharge of oxygen is needed to prevent the reduction of the film during the interruption. On some specimens, after a few seconds' interruption, small oxygen bubbles continued to stream from certain points after they had ceased to come off from the specimen as a whole; if, at this stage, the circuit was restored, small bubbles continued to rise from the points in question, although elsewhere the electrode became rapidly attacked. In such cases the strength of current passing was intermediate between the ordinary active and passive values.

The irregular behaviour of the air-exposed electrodes provided another example of the variable character of the film produced by the action of air at low temperatures; on some specimens, a weak point would chance to be included in the electrode area, whilst on others there would be no spots sufficiently faulty to cause breakdown under the prevailing conditions. Specimens exposed to *M*/10-potassium chromate for five days evidently possessed a more uniform skin; without exception, these behaved as "passive" electrodes, provided that the circuit was completed before the specimen was introduced into the acid. Immersion in *M*/10-chromic acid for the same period afforded even better protection; here it was possible to place the specimen in the acid for short periods before the current was turned on, and yet to obtain oxygen evolution immediately the circuit was completed. In four experiments in which the current was started respectively 1, 1, 2, and 4 seconds after immersion, passivity was obtained; but in a fifth experiment, where a period of 5 seconds was attempted, the electrode had become active.

The objections raised to the "film theory" of anodic passivity in acid solutions can thus be answered as follows.

- (1) The statement that the oxide film on iron is rapidly destroyed

by acid is true of ordinary conditions, but not of anodic conditions. Under suitable anodic conditions, these films are unaffected by the acid (best observed if the films are thick enough to produce interference tints).

(2) The statement that the nature of the film does not affect the time which elapses before passivity appears is only true of experiments in which the film is dissolved away before the current is turned on. If the circuit is completed before introduction of the specimen, the nature of the film may make all the difference between immediate passivity and serious corrosion.

(3) The statement that iron rendered passive by anodic treatment behaves differently from iron rendered passive, *e.g.*, by simple immersion in a chromic acid solution is perfectly true; the reason is clearly found in the fact that the anodically polarised iron possesses a supercharge of oxygen, which serves to keep the oxide film repaired and in the fully oxidised condition.

Experiments conducted at higher current densities, which permitted the electrode to revert to the passive state after once it had become active, confirmed several of the observations of W. J. Müller (*Z. Elektrochem.*, 1927, 33, 401; 1928, 34, 572; 1929, 35, 656) and of Hedges (*J.*, 1926, 2878; 1927, 2710; 1928, 969). A visible brown coat often appeared on the electrode prior to the arrival of oxygen bubbles; if, for any reason, this brown coat appeared first at one particular region, bubbles were subsequently observed first at that region; in general, the evolution of bubbles started first at the bottom, and spread upwards, producing the U-shaped area described by Hedges. W. J. Müller is undoubtedly right in thinking that saturation of the liquid with ferrous sulphate must be attained before passivity can set in; the difficulty of obtaining passivity with vertical electrodes is explained by the fact that heavy ferrous sulphate solution—clearly distinguishable by reason of its different refractive index—sinks continuously down from the anode, and this circulation hinders the attainment of saturation.

*Principles governing Anodic Passivity in Acid Solution.*—When a metal is subjected to anodic treatment, its surface layers are converted *in situ* into a compound with the principal anion of the liquid. If this compound is freely soluble, it will dissolve, exposing a fresh surface of metal to attack; but if sparingly soluble, it will remain *in situ*, protecting the underlying metal. Thus, lead in a sulphate solution, silver in a chloride solution, and iron in a hydroxide solution escape attack almost from the first; the protective layer, being in optical contact with the metal, is frequently invisible. But ferrous sulphate is readily soluble, and a film-free iron anode in a sulphuric acid solution will dissolve freely at first. If, however, the layer of liquid



next to the metal should become saturated with ferrous sulphate, the behaviour of iron will be analogous to that of lead, and if now the surface portions are converted into sulphate, this will no longer dissolve and will temporarily protect the metal. This *protective* sulphate is probably invisible; it is fairly certain that the visible deposit is not the protective layer, but the result of spontaneous crystallisation of hydrated sulphate from the liquid which is locally supersaturated with respect to that salt; its importance lies in furnishing a sure sign that saturation has been reached. When once the whole anode surface is converted into sulphate, any further discharge of  $\text{SO}_4^{--}$  ions cannot cause further attack on the iron, and must (as on a platinum anode) lead to evolution of oxygen. The bubbles of oxygen, however, will soon stir up the liquid, and the visible layer will gradually dissolve or flake off (a phenomenon observed by Hedges and by W. J. Müller). Meanwhile, however, the metal will have become supercharged with oxygen, and, at high current densities, this may be sufficient to produce and maintain an oxide film on the surface which (as shown) will *not* be dissolved by the acid under anodic conditions; in that case passivity will persist indefinitely, and the current will be expended on the production of oxygen. At lower current densities, the oxide film may not be maintained, and the electrode may revert to the freely dissolving condition; if so, periodicity may be set up. At still lower current densities, a state of saturation in the anodic layers will never be reached and the electrode will remain active indefinitely; this is most likely to occur if the conditions are favourable to convection.

A theory that the anodic passivity of iron in a sulphate solution may be initiated by a protective layer of *ferric* sulphate has been put forward by McCulloch (*Trans. Amer. Electrochem. Soc.*, 1929, 56, 325). He points out that ferric sulphate dissolves only slowly in water, and that such a film might persist even in unsaturated solution. McCulloch is undoubtedly right in thinking that salts, as well as oxides, may constitute protective films. Moreover, it is not impossible that the slow dissolution of ferric sulphate by water may itself be the cause of the slow dissolution of ferric oxide film by dilute sulphuric acid; but it is not easy to explain the facts set forth above on the hypothesis that the protection is due solely to a film of ferric sulphate.

*Function of Carbon Dioxide in Corrosion by Condensed Moisture.*—Many early workers and one recent writer (Fujihara, *Chem. Met. Eng.*, 1925, 32, 810) have ascribed to carbon dioxide a special rôle in rusting; this idea may have arisen from the serious damage produced by the combustion products of coal, now commonly attributed to oxides of sulphur. The researches of Dunstan, Jowett,

and Goulding (J., 1905, **87**, 1548), Tilden (J., 1908, **93**, 1356), and Hicks (*J. Physical Chem.*, 1929, **33**, 781) have definitely proved that the presence of carbon dioxide or other acidic substance is not necessary for rusting; but the measurements of Hicks indicate that moist oxygen does produce rust more quickly if carbon dioxide also is present.

Apart from the scientific, historical, and economic interest of the matter, the question whether carbon dioxide—in amounts normally present in air—constitutes a serious cause of corrosion is important to experimenters, since the detailed observation needed for detection of vital microscopic occurrences becomes almost impossible if the work has to be conducted exclusively in closed vessels. Some experiments have, therefore, been performed to elucidate this point.

Specimens, 5.5 cm. square, were degreased with carbon tetrachloride and then alternately ground and degreased three times. Into each of a series of beakers, 8.5 cm. high and 4 cm. in diameter, a small quantity of water (2 c.c. in the main series) was placed, and one of the specimens was cemented over the mouth of each beaker with nitrocellulose. After the seal had set, the bottoms of the beakers were placed in warm water (50°), and a metal dish containing ice was placed on the upper side of the specimen. Water then distilled without ebullition, condensing on the lower side of the specimen in droplets, fairly large in the centre and microscopic around the edges. In other parallel experiments saturated carbon dioxide solution or *N*/100-sodium hydroxide solution was used instead of water; four different materials were employed, *viz.*, steel H 28, electrolytic iron E 28, commercial zinc containing lead, and electrolytic zinc; abrasion with four different grades of emery, and also scraping with a knife, was studied in different series.

The fact that the presence of carbon dioxide may affect results is clearly shown by the experiments on zinc: the distillate from dilute alkali produced, in practically every drop, a microscopic circle or sphere of membranous zinc hydroxide surrounding a tiny dark point representing the seat of corrosion; in the presence of carbon dioxide, however, the white hydroxide did not appear, but there was general darkening of the metal.

On iron and steel, the result was identical whether distillation was conducted from *N*/100-sodium hydroxide, distilled water, or carbon dioxide solution; in every case, some of the drops developed rust, whilst others remained perfectly clear. On many specimens, the frequency of rust-developing droplets varied from one part to another in a manner not depending on the drop size. Thus no accurate count could be made of the proportion of drops developing

rust, but this appeared to be highest in the coarsely abraded specimens. There was no evidence that the presence of carbon dioxide increased the probability of rust formation in a drop, although, where rust appeared at all, it seemed to be developed more quickly if carbon dioxide was present, thus confirming Hicks's results. After time had been allowed for the development of rust in those drops which were able to produce it, the specimen could be taken off the beaker and exposed to a stream of carbon dioxide (or to carbon dioxide and air alternately) without causing any rust in the clear droplets; indeed the specimen could conveniently be dried in a stream of carbon dioxide without fear of increasing the number of rust spots. Apparently the presence of carbon dioxide is incapable of causing rusting in places which have escaped rusting in its absence. On the other hand, exposure to the vapour of hydrochloric acid for only 15 seconds caused rapid rusting, in the places which had previously escaped. There seems no doubt that the corrosive qualities of the air of many laboratories—frequently attributed to carbonic acid—are really due to other acids.

The observations are explained by the fact that iron specimens are covered with an invisible film of ferric oxide with irregularly distributed weak spots (Evans, J., 1929, 117). The chance of rust formation will depend on the "probability" that the drop area includes a place on the skin sufficiently "weak" to admit the most penetrating anion present. In pure water this will be the hydroxyl ion, and the ferrous hydroxide formed as the anodic product will interact with dissolved oxygen at a distance to form the less soluble ferric hydroxide ("rust"). The presence of carbon dioxide will certainly not increase the probability of initiation of rusting, since it is unlikely to dissolve the film of ferric oxide, whilst it will decrease the hydroxyl-ion concentration; the penetrating power of the  $\text{HCO}_3^-$  or  $\text{CO}_3^{--}$  ions can probably be neglected. But if it be assumed that the weak spot *does* exist under a droplet, the carbon dioxide may accelerate the electrochemical action, by enhancing the conductivity and hydrogen-ion concentration.

In some of the early experiments, a small proportion of the previously rust-free droplets developed rust after the vessels were opened; this may have been due to traces of acid fumes, but was probably due to the bending that accompanied opening. It was found that if a specimen was cut with small shears when the droplets were in position, the drops near the shear-lines, although quite untouched by the shears, quickly developed rust, clearly because the cutting stresses fractured the protective film.

Droplets produced by distillation from ammonia caused no true rust, evidently owing to the presence of sufficient alkali to depress

the solubility of ferrous hydroxide; some attack did occur, however, since, after the drops had been removed by evaporation, interference tints were noticed.

It was observed (before the opening of the vessels) that droplets which developed rust tended to "dry up"—partially or completely—and that the clear drops situated close to a drop which had developed rust frequently disappeared altogether; on the other hand, in regions where no rust appeared, the drops showed no signs of evaporation. This confirms the early view of Crum Brown (*J. Iron Steel Inst.*, 1888, ii, 129) that rust is essentially hygroscopic—a matter recently discussed by Hudson and others (*Trans. Faraday Soc.*, 1929, 25, 207, 485, 487, 493).

*Corrosion of Iron immersed in a Carbonic Acid Solution.*—Some confusion exists regarding the effect of carbon dioxide in "immersed corrosion." In *hard, natural* waters containing calcium bicarbonate, it is unquestionable that excess of carbonic acid increases the corrosive character; in the absence of free carbonic acid such waters, when they act on iron, necessarily deposit calcium carbonate on the cathodic areas, and the deposit obstructs diffusion of oxygen, bringing the action to a standstill (Tillmans and Klarmann, *Z. angew. Chem.*, 1923, 36, 94, 103, 111, 113; Baylis, *Ind. Eng. Chem.*, 1927, 19, 177; Evans, *J. Soc. Chem. Ind.*, 1928, 47, 57T); in the presence of excess of carbonic acid, this deposition does not occur, and the corrosion continues. The indirect action of "aggressive" carbon dioxide may be serious even with metals where its direct action is undoubtedly inhibitive; thus the corrosion of lead by distilled water is retarded by the presence of carbon dioxide, but waters containing sufficient calcium bicarbonate to have no permanent action on lead become distinctly plumbosolvent if much excess carbon dioxide is present.

The action of dissolved carbonic acid *in the absence of calcium compounds* is quite different. The normal product is soluble ferrous bicarbonate, as indicated by Crum Brown (*loc. cit.*); the bicarbonate is formed very quickly if the carbon dioxide is under 50 atm. pressure (E. Müller and Henecka, *Z. anorg. Chem.*, 1929, 181, 159), but at ordinary pressures the action is much slower, quite small quantities of iron rendering the liquid supersaturated with respect to ferrous carbonate (Tillmans and Klarmann, *loc. cit.*). If oxygen is present, the iron is likely to be precipitated as ferric hydroxide (rust) in a form which will hinder diffusion; indeed Bauer's tests (*Stahl u. Eisen*, 1921, 41, 37, 76) indicate that distilled water containing carbon dioxide may produce less corrosion than distilled water free from carbon dioxide, owing to the obstructive character of the rust produced.

To elucidate this matter further, new experiments have been performed. A number of strips of iron H 28, 2 cm. wide, were cut, abraded, degreased, and immersed vertically to a depth of 4 cm. for 15.5 hours at 14° in 65 c.c. of liquid in beakers 8.5 cm. high and of 4 cm. diameter. The loss of weight produced by different liquids is shown in Table II; it will be noticed that within this time saturated carbon dioxide has produced more corrosion than distilled water but much less than *M*/20-sulphuric acid; the water "condensed on silica" was a sample prepared by L. C. Bannister and S. C. Britton for work on electrode potentials, the special object being to exclude traces of metals.

TABLE II.

Liquid.	Loss of weight, mg.			Mean, mg.
<i>M</i> /20- $K_2SO_4$ .....	2.9,	3.3,	3.5	3.2
<i>M</i> /20- $H_2SO_4$ .....	20.1,	20.5,	20.6	20.4
Saturated $CO_2$ solution .....	5.9,	7.0,	7.0	6.6
Laboratory distilled water .....		1.5,	1.7	1.6
Laboratory distilled water, redistilled and condensed on silica .....		1.0,	1.3	1.1

A series of qualitative experiments, interrupted at different stages, showed the action of carbonic acid solution to be as follows. Freshly immersed specimens are attacked by carbonic acid just as by any dilute acid, hydrogen being evolved slowly; the bubbles appear mainly at the edges and a few favoured spots on the faces (evidently points of low over-potential); but the actual attack commences at quite different points (evidently weak spots on the skin). For a time the liquid remains clear, though containing a considerable quantity of iron dissolved as ferrous bicarbonate; after about 2 hours, rust (ferric hydroxide) begins to appear along the water-line, and gas evolution gradually ceases, as the  $p_H$  value rises from about 4.0, where hydrogen production is appreciable, to a range (5.0—6.0) where direct hydrogen evolution is almost negligible. Meanwhile the oxygen absorption type of attack is increasingly hindered by the formation of rust over the water-line zone. The conditions thus become less favourable for corrosion than in a neutral sulphate or chloride solution, where the corrosion is of the differential aeration type from the first moment, and where the cathodic zone near the water-line remains comparatively free from rust, so that oxygen can continue to reach the place where it is required for corrosion. It is to be expected, therefore, that over long tests carbonic acid would produce a smaller amount of corrosion than a salt solution; and it was found in a 39-day test by the author (*J. Soc. Chem. Ind.*, 1928, 47, 77r) that actually the corrosion by saturated carbonic acid was less than that produced by *M*/20-

sodium sulphate or chloride. Probably Bauer's results, mentioned above, can be explained in the same way. In effect, carbonic acid solution is not a serious corroding agent.

It would appear that, with carbonic acid, the "hydrogen-evolution type" of corrosion lasts just long enough to produce rust at a point unfavourable to subsequent attack of the "oxygen-absorption type." The apparent exhaustion of hydrogen ions occurs long before the quantity of iron dissolved is stoichiometrically equivalent to the carbonic acid present; some experiments conducted with sulphuric acid showed that here the attack persists rapidly even when most of the acid has been used up. The difference between the action of sulphuric and carbonic acids is easily understood by considering the movement of  $p_H$  during titration of these acids with alkalis; with sulphuric acid, the  $p_H$  value remains very low (below 3.0) until the end-point is approached, whereupon it suddenly rises; with the weak carbonic acid, the  $p_H$  value is higher at the first (about 4.0) and commences to rise even with the first addition of alkali. The  $p_H$  value alters in much the same way when the acid is used up on the corrosion of iron; thus sulphuric acid continues to evolve hydrogen almost to the last, whilst with carbonic acid, the evolution of hydrogen—weak even from the first—soon dies away.

The rapid exhaustion of carbonic acid stands in contrast to the view of Crum Brown (*loc. cit.*) that a limited quantity of carbonic acid "can carry on the process indefinitely," being regenerated in full when the ferrous bicarbonate is oxidised to ferric hydroxide. Actually the conception of "regeneration in full" is inadmissible, since the precipitation of ferric hydroxide is inconsistent with concentrations of hydrogen ions such as are present in pure water saturated with carbon dioxide at normal pressure. Only if the concentration of carbon dioxide is kept low, can ferric hydroxide be produced. Since, however, the oxidation of ferrous bicarbonate to the ferric condition occurs at the water-line, the dissociation of any ferric carbonate that may temporarily be formed is quite to be expected, the carbon dioxide passing out into the gas phase (where the partial pressure of carbon dioxide is usually low) as quickly as oxygen is taken in. This accounts for the fact that, in 24-hours experiments, practically no carbonate was found in the "rust," which was mainly hydroxide, and practically no free carbon dioxide was found in the liquid, although this still contained much ferrous iron in solution. The facts do not support Crum Brown's idea of the cyclic regeneration of carbonic acid.

Recently, theories based on liberation of acid by hydrolysis of ferric salts have been suggested for other types of corrosion.

McCulloch (*Trans. Amer. Electrochem. Soc.*, 1929, 55, 268) considers that, in corrosion by chloride solution, the ferrous chloride first produced "may be oxidized to ferric chloride by absorption of oxygen, and ferric chloride may hydrolyze to give hydrochloric acid. This hydrochloric acid may attack the steel." It seems difficult to understand how any considerable increase of acidity can be produced by the action of oxygen on ferrous chloride, since in addition to ferric chloride, this oxidation itself must produce ferric hydroxide or basic ferric chloride. Whilst the hydrolysis of ferric salts undoubtedly is responsible for the formation of rust in the final stages of the action of acids on metals, it is doubtful whether regeneration of acid plays any serious part in prolonging the attack.

### *Summary.*

Chromic acid has strong oxidising and weak base-dissolving properties; it produces passivity when present alone, but stimulates corrosion if sulphuric acid also is present.

The ferric oxide film usually present on iron is rapidly destroyed by dilute sulphuric acid owing to the formation of the circuit iron|acid|oxide; the ferric oxide suffers cathodic reduction to ferrous oxide, which is rapidly dissolved by the acid. If the reduction is prevented by the presence of excess of chromic acid, or by anodic treatment of the specimen as a whole, the film can remain in contact with  $M/10$ -sulphuric acid for hours without change. This explains why iron can remain passive in acid solution during anodic treatment.

The explanation of anodic passivity in acid solution is as follows. When lead is anodically treated in sulphuric acid, the conversion of the metallic surface into sulphate will protect the metal below, but with an iron anode this will only occur when the liquid has locally become saturated with ferrous sulphate. At that stage, any further current must be expended on the production of oxygen, and although the bubbles stir the liquid, dispelling the saturated layer, the metallic surface may in the meanwhile have been converted into ferric oxide, which will protect the metal so long as the current continues to flow. Indeed, a short interruption of current can also be tolerated without resumption of activity, and this seems to depend on the presence of an oxygen supercharge, which prevents reduction to the rapidly soluble lower oxide.

The corrosive qualities of carbon dioxide have been exaggerated in the past, and probably the damage attributed to carbon dioxide has really been due to sulphur dioxide or hydrogen chloride. If water is allowed to condense in droplets on iron, some of them develop rust, whilst others (which do not happen to rest on a weak point) remain clear; this is true whether carbon dioxide is present

or absent, and the clear drops may be dried up in a current of carbon dioxide without developing rust; hydrogen chloride vapours quickly produce rusting. A solution of carbonic acid causes at first slight corrosion of the hydrogen-evolution type, but the  $p_H$  rapidly rises and the formation of hydrogen ceases; the ferrous bicarbonate produced yields ferric hydroxide at the water-line, and this obstructs diffusion of oxygen and prevents attack of the oxygen-absorption type. In effect, therefore, a solution of carbonic acid is not dangerously corrosive; but it must be remembered that the presence of excessive free carbonic acid in a hard natural water may prevent the deposition of calcium compounds which would otherwise bring the action to a standstill.

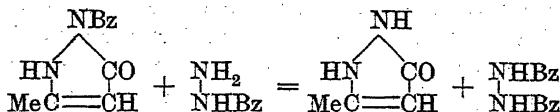
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## LXVII.—N-Acylpyrazolones as Acylating Agents.

By JOTI SARUP AGGARWAL and JNANENDRA NATH RAY.

ETHYL acetoacetate reacts with benzoylhydrazine at  $100^\circ$ , s-di-benzoylhydrazine and 3-methyl-5-pyrazolone being formed. Their production may be explained by the fact that 1-benzoyl-3-methyl-5-pyrazolone, which can be isolated when the above condensation is carried out at  $10-16^\circ$ , reacts readily with compounds containing an amino-group, 3-methyl-5-pyrazolone and the benzoyl derivative of the amine being formed.



Under the same conditions, benzoylhydrazine does not benzoylate a primary amine.

Similar results are obtained when phenylacetylhydrazine is substituted for benzoylhydrazine in the above reactions.

Bongert (*Compt. rend.*, 1901, **132**, 973) has obtained 3-methyl-5-pyrazolone and butyrylhydrazine by the interaction of methyl  $\beta$ -butyryloxyacrylate and hydrazine.

### EXPERIMENTAL.

*Interaction of Phenylacetylhydrazine and Ethyl Acetoacetate. Formation of s-Diphenylacetylhydrazine and 3-Methyl-5-pyrazolone.*—Phenylacetylhydrazine (7.5 g.), ethyl acetoacetate (6.5 g.), absolute alcohol (1.3 c.c.), and 3 or 4 drops of piperidine were heated together



on the steam-bath for 3 hours. The solid product was extracted with hot water, and the residue crystallised from absolute alcohol, colourless needles of *s*-diphenylacetylhydrazine (4.0 g.), m. p. 232—233°, being obtained; Pinner and Gobel (*Ber.*, 1897, **30**, 1889) give m. p. 231° (Found: N, 10.65. Calc. for  $C_{16}H_{16}O_2N_2$ : N, 10.4%). The aqueous extract on concentration gave 3-methyl-5-pyrazolone, m. p. (after recrystallisation) and mixed m. p. with an authentic specimen, 215°.

*s*-Dibenzoylhydrazine.—A mixture of benzoylhydrazine (7 g.), ethyl acetoacetate (6 g.), alcohol (2 c.c.), and piperidine (3 or 4 drops) was heated on the steam-bath as in the preceding case. The product, isolated in a similar way and recrystallised from alcohol, gave colourless plates (3.5 g.), m. p. 235°, of *s*-dibenzoylhydrazine (Struve, *J. pr. Chem.*, 1894, **50**, 299, gives m. p. 233°) (Found: N, 11.8. Calc. for  $C_{14}H_{12}O_2N_2$ : N, 11.7%).

1-Phenylacetyl-3-methyl-5-pyrazolone.—A mixture of phenylacetylhydrazine (7.5 g.), ethyl acetoacetate (6.5 g.), and piperidine (3 or 4 drops) was kept at the ordinary temperature for 12 hours. The solid product crystallised from hot xylene in pale brownish needles, m. p. 134—136° (Found: N, 13.3.  $C_{12}H_{12}O_2N_2$  requires N, 13.0%). A small quantity of a substance, m. p. 228—230°, insoluble in hot xylene was not investigated.

1-Phenylacetyl-3-methyl-5-pyrazolone (0.8 g.) was heated with an equivalent quantity of aniline at 130—140° for an hour or at 100° for 3 hours. Phenylacetanilide, m. p. 116° after recrystallisation, was isolated from the reaction mixture, and 3-methyl-5-pyrazolone from the acid extract (see below).

Phenylacetanilide.—A mixture of phenylacetylhydrazine (5 g.), ethyl acetoacetate (4.3 g.), and a few drops of piperidine was kept over-night, aniline (3 g.) added, and the mixture heated at 130—140° for an hour. The cooled mass was ground with dilute hydrochloric acid, the liquid filtered, and the residue extracted with tepid alcohol. The alcoholic extract on concentration and dilution with water furnished phenylacetanilide (1.9 g.) which, after recrystallisation from hot dilute alcohol, melted, alone or mixed with an authentic specimen, at 116°; a further quantity (0.9 g.) was isolated, by fractional crystallisation, from the residue from the alcohol extraction.

A mixture of phenylacetylhydrazine (3 g.) and aniline (2 g.), heated at 130° for 1 hour, gave no phenylacetanilide.

LXVIII.—*The Vapour Density of Zirconium Tetrachloride.*

By JOHN ALBERT NEWTON FRIEND, ALBERT THOMAS WILLIAM COLLEY, and RICHARD SIDNEY HAYES.

THE only published data on the vapour density of zirconium tetrachloride appear to be those of Deville and Troost (*Compt. rend.*, 1857, 45, 821), who, using Dumas's method at the boiling point of sulphur, obtained the values 8.10 and 8.21 (Calc. : 8.09; air = 1). These results were of particular interest at the time, since they indicated that zirconium was quadrivalent, in opposition to the general belief in its trivalency. The second value for the density is somewhat greater than the theoretical. Apart from error of observation, this might be accounted for by the presence of hafnium, although the possibility of association of the tetrachloride deserves consideration.

During experiments on the volatilisation of pure zirconium tetrachloride in a current of chlorine, it had frequently been observed by one of us that brown fumes were formed characteristic of zirconium trichloride (Ruff and Wallstein, *Z. anorg. Chem.*, 1923, 128, 96). It seemed of interest, therefore, (i) to determine if association could be detected in the vapour at temperatures only slightly above that at which volatilisation begins, and (ii) to follow up the observed dissociation into trichloride at higher temperatures with vapour-density measurements.

## EXPERIMENTAL.

*Purification of Materials.*—Elimination of hafnium was effected by a method based on the observation that zirconium is more readily precipitated from solution by citric acid than is hafnium (Drophy and Davey, *Physical Rev.*, 1925, 25, 882). A sample of "pure" zirconia was converted into sulphate by heating with concentrated sulphuric acid, and the solution diluted and filtered. The hydrated oxide was precipitated with ammonia from the boiling solution, washed, and dissolved in pure nitric acid; the clear solution was evaporated to dryness, the residue dissolved in water and filtered, and citric acid added in sufficient amount to precipitate about half the zirconium as citrate, any hafnium together with the remainder of the zirconium being retained in solution. The precipitate was filtered off, washed, ignited to oxide, and the process repeated. A very pure sample of zirconia was thus obtained.

*Test for cerium.* The following test for traces of ceria in zirconia was found useful. Cerium colours a borax bead yellowish-green

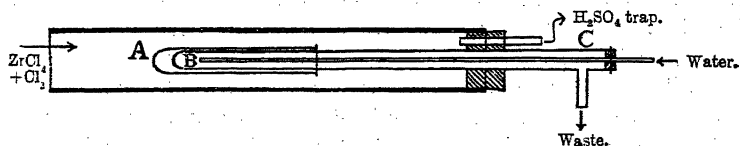
when heated in the oxidising flame. A borax bead weighing 0.056 g. was perceptibly coloured (in daylight) by 0.0015 g. of zirconia containing 4% of ceria.

*Purity of the zirconia.* Several attempts were made to follow the elimination of hafnia from zirconia by density measurements (Hevesy, J., 1924, 125, 2372). The results, however, were not sufficiently concordant to be of service, possibly owing to the mechanical loss of oxide during ignition, which it is extraordinarily difficult to avoid (see Venable and Bell, *J. Amer. Chem. Soc.*, 1917, 39, 1599). The equivalent of the zirconium was therefore determined chemically from the ratio  $\text{Zr}(\text{SO}_4)_2 : \text{ZrO}_2$ . A weighed quantity of the purified zirconia was heated with concentrated sulphuric acid for at least an hour. The rate of solution of the oxide was found to depend upon its previous history, frequent ignition rendering it very refractory. In none of our experiments were we able to effect complete solution of the sample taken. After cooling, the mixture was poured into excess water, and heated to boiling, any undissolved zirconia being filtered off, ignited, and weighed.

The solution of zirconium sulphate was evaporated to dryness in a platinum dish, the heating being carefully controlled towards the close of the experiment in order to drive off the excess of acid without decomposing the sulphate. When a constant weight had been obtained, the temperature was raised and the sulphate ignited to oxide. In every case the weight of oxide thus obtained was slightly less than that originally dissolved, presumably owing to mechanical loss. For instance, in two experiments, the initial weights of zirconia were 0.4051 and 0.2707 g. and the final weights 0.3926 and 0.2687 g. respectively. As calculated from the initial weights, the values obtained for the equivalent weight of zirconium were 22.04, 22.00, mean 22.02; the accepted value for 1929 being  $91.2/4 = 22.8$ . Our value is somewhat low in common with early atomic-weight determinations by this method [compare Weibull (*Lund. Årsskrift*, 1881—1882, vol. xviii), who obtained the mean value of  $89.54/4 = 22.39$ ], probably owing to the difficulty of completely expelling the acid without simultaneously decomposing the sulphate. The results, however, indicate the absence of appreciable quantities of hafnium.

*Preparation of Zirconium Tetrachloride.*—This was effected by Demarçay's method (*Compt. rend.*, 1887, 104, 1136), viz., by passing chlorine, laden with carbon tetrachloride vapour and dried by phosphoric oxide, over heated zirconia as described by Venable and Bell (*loc. cit.*). The chloride was collected in a long tube and transferred by shaking into a bottle. It invariably contained traces of zirconia

carried over mechanically. To obtain the pure chloride, the first batch was returned to the apparatus and re-sublimed in a very slow current of chlorine—about 2 bubbles per second, as recommended by Lely and Hamburger (*Z. anorg. Chem.*, 1914, 87, 223). Since the tetrachloride is very susceptible to moisture, it was condensed on tube A (see fig.), which easily slid over the water-cooled tube BC. When sufficient had collected, BC was withdrawn and A rapidly slid into a slightly wider tube, which thus enclosed the tetrachloride. After being weighed, this double tube was used as the dropping bottle in the Victor Meyer apparatus. It was ascertained that no condensation of carbon tetrachloride took place along with the zirconium salt under our experimental conditions.



Venable and Bell state that formation of chloride in their experiments began a little above  $300^{\circ}$  and was rapid at  $450$ – $500^{\circ}$ , though Lely and Hamburger found it necessary to employ a temperature of  $800^{\circ}$  to obtain the chloride in bulk. We attempted to determine the lowest temperature by passing chlorine and carbon tetrachloride vapour over zirconia in a tube supported vertically in a metal-bath, the temperature of which was slowly raised, and noting the first appearance of sublimate. This occurred at  $355^{\circ}$ , but the whole of the oxide was not converted into chloride even at  $500^{\circ}$ . The temperature necessary evidently varies with the physical condition of the oxide.

*Determination of Vapour Density.*—A modification of Victor Meyer's apparatus was used, the heated portion consisting of a silica vaporising tube of 350 c.c. capacity, supported vertically in an electric furnace. The upper part of the apparatus was of glass and fitted into the silica tube with a ground joint lubricated with phosphoric acid. The whole was thoroughly dried, and the vertical portion filled with dried chlorine. Traces of moisture were rigidly excluded, as they reduced the vapour density enormously. In all the experiments at  $700^{\circ}$  the sublimate in the tube at the close of the tests was tinged with brown.

The results are given below, the vapour density being referred to that of air as unity.

		At $400^{\circ}$ .		At $445^{\circ}$ .	
ZrCl <sub>4</sub> , g. ....	0.0875	0.0842	0.0396	0.0890	0.0880
V.D. ....	7.32	7.83	6.96	5.94	6.30

At 500°.

ZrCl <sub>4</sub> , g.	0.1271	0.1215	0.1105	0.1100	0.1051	0.1042	0.0974	0.0894	0.0425
V.D.	8.81	6.18	7.50	6.42	9.18	9.25	8.52	7.94	6.20

At 700°.

ZrCl <sub>4</sub> , g.	0.1362	0.0790	0.0762	0.0626	0.0613	0.0584	0.0444	0.0430	0.0253
V.D.	9.00	4.51	5.68	5.26	4.78	7.64	3.81	4.68	4.13

*Conclusions.*—Consideration of the results shows that (1) there is no evidence of association at 400° or above. The four high results at 500° and the one at 700° are believed to be due to decomposition as indicated below. (2) The vapour density of zirconium tetrachloride in chlorine falls with rise of temperature, and appears to fall slightly with dilution. Presumably the vapour first dissociates into the trichloride and free chlorine,  $2\text{ZrCl}_4 \rightleftharpoons 2\text{ZrCl}_3 + \text{Cl}_2$ . The decomposition can hardly end there, however, since according to Ruff and Wallstein (*loc. cit.*) the trichloride also dissociates above 330°, thus:  $2\text{ZrCl}_3 \rightleftharpoons \text{ZrCl}_4 + \text{ZrCl}_2$ ; moreover, above 600° the dichloride deposits zirconium,  $2\text{ZrCl}_2 = \text{ZrCl}_4 + \text{Zr}$ . The reactions in the vaporising tube may thus be very complex and it is not regarded as possible that a complete equilibrium could be obtained in the brief course of an experiment.

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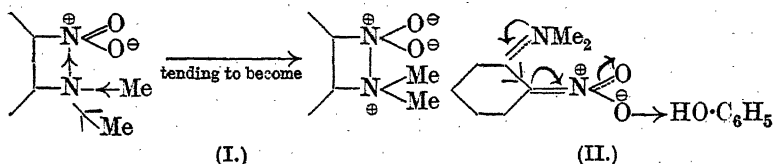
## LXIX.—3-Halogeno-6-nitro- and -6-amino-dimethylanilines.

By HERBERT HENRY HODGSON and ARNOLD KERSHAW.

THE 2:4-dihalogenonitrobenzenes have been found to react readily with an alcoholic solution of dimethylamine in the absence of a catalyst, and in every case it is the 2-halogeno-substituent that is easily and exclusively replaced by the dimethylamino-group, this being in accordance with the well-known promotion of mobility of halogens by an adjacent nitro-group. Further, the ease of replacement of one halogen only, indicates considerable satisfaction of the electronic demands of the nitro-group by one dimethylamino-group (compare the ease with which sodium methoxide replaces both halogens in a 2:4-dihalogenonitrobenzene, a further illustration of the fact that  $\text{NMe}_2 > \text{OMe}$  as a potential electron-source). It is noteworthy also that in 4-chloro-2-iodonitrobenzene the iodine only is replaced by dimethylamine under the same conditions, a fact which indicates that the 2-carbon atom is more positive than the

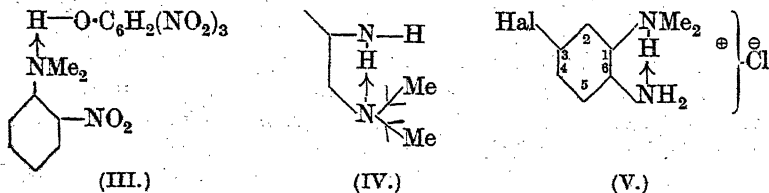
4-carbon atom, notwithstanding the greater positivity produced by chlorine as compared with iodine, and therefore that the general effect of the nitro-group (Allan, Oxford, Robinson, and Smith, J., 1926, 401) is much greater on the 2-carbon than on the 4-carbon atom.

Most unsubstituted 2-nitrodialkylanilines are liquids at the ordinary temperature, but the derivatives now under consideration are solids of low m. p., and since the *p*-nitrodialkylanilines have high m. p.'s (*e.g.*, 4-nitrodimethylaniline has m. p. 168°), it is probable that the low m. p.'s of the *o*-compounds are due to co-ordination of a similar type (I) to that described by Bennett and Willis (J., 1929, 256).



The 3-halogeno-6-nitrodialkylanilines are not sufficiently basic to form salts except with strong acids, and these are immediately hydrolysed by water. In non-dissociating solvents such as light petroleum and naphthalene, 1% solutions are yellow, and the molecular weight of 3-chloro-6-nitrodialkylaniline in naphthalene is about 10% above that of the single molecule (compare the discussion of similar cases by Sidgwick, "Electronic Theory of Valency," 1927, p. 149 *et seq.*, who considers that such cryoscopic evidence of association must be interpreted with caution). Very deep red 1% solutions are formed in phenol, the product being unimolecular, which might reasonably indicate a change of structure produced by co-ordination of solvent (II). Anisole does not give this colour change.

The picrates of the 3-halogeno-6-nitrodialkylanilines are stable, with m. p.'s below those of the 3-halogeno-6-aminodimethylanilines: these are true salts soluble in water, so the diminution of melting point may be due to chelation (III)—a point of view which is supported by the fact that the more salt-like is the picrate of a 3-halogeno-6-nitrodialkylaniline the higher is its m. p.; *e.g.*, iodo- (104°), bromo- (85°), and chloro- (70°), a series conforming with the well-known order of the general effects of the halogens, Cl > Br > I.



The 3-halogeno-6-aminodimethylanilines are all liquids at the ordinary temperature, owing doubtless to chelate union (IV) (compare Sidgwick and Callow, J., 1924, **125**, 527), which should be stronger than in the case of *o*-phenylenediamine (m. p. 102°), since the dimethylamino-nitrogen is more negative than the amino-nitrogen atom. Moreover, the free bases, including *o*-aminodimethylaniline itself, are much more stable in air than *p*-aminodimethylaniline and much less soluble in water: this is further evidence of the great stability associated with 5-membered chelate rings.

All the above substances form stable monohydrochlorides; but only the halogeno-compounds give dihydrochlorides, which diminish in stability from the chloro- to the iodo-compound. It would appear that salt formation produces in the monohydrochloride of *o*-aminodimethylaniline a 5-membered chelate ring, by the sharing of a hydrogen ion between the amino-groups (V) (compare Sidgwick's discussion on hydrofluoric acid, *op. cit.*, p. 72), which is sufficiently stable to prevent further salt-formation at the amino-nitrogen atom; but that when the 3-halogeno-atom is introduced, its general (inductive) effect on the chelating electrons of the *p*-amino-nitrogen atom is a weakening of their union to such an extent that, under the influence of the powerful kationoid reagent (a second molecule of hydrochloric acid), the dimethylamino-group captures the hydrogen atom and thus enables further salt formation to take place at the released amino-group. This salt formation is facilitated by the alternating (tautomeric) effect of the halogen substituent, now rendered available (compare the greater positivity of the 3-carbon atom in comparison with the 4-carbon atom in activated 1-chloro-3:4-dinitrobenzene, due to the alternating effect of the chlorine atom). Since the order of the general effect of the halogens is  $\text{Cl} > \text{Br} > \text{I}$ , it follows that 3-chloro-6-aminodimethylaniline dihydrochloride will be the most easily formed and, in consequence, be the most stable of the analogues.

Only the free bases mentioned above give violet colours with ferric chloride; the salts, however, do so with stronger oxidising agents (*e.g.*, chromic acid).

3-Chloro-6-aminodimethylaniline was recovered unchanged after repeated treatment with Caro's acid under widely varying conditions: this resistance to oxidation is probably due to chelation both in the free base and in the salt (compare the ready oxidation of *o*-anisidine and *o*-nitroaniline to the corresponding nitroso-derivatives, and the instantaneous destruction of *p*-aminodimethylaniline under the same conditions).

## EXPERIMENTAL.

*Action of Dimethylamine on the 2:4-Dihalogenonitrobenzenes.*—The 2:4-dihalogenonitrobenzene (10 g.) was boiled under reflux with 10% more than the theoretical quantity of a solution of dimethylamine (1 g.-mol.) in ordinary alcohol (400 c.c.) to which an equal volume of the solvent had been added. The chloro- and bromo-compounds were refluxed for 10 hours and the iodo-analogue for 15 hours, the alcohol then being removed by steam; the oily reaction product solidified on cooling [compare Weissenberger (*Monatsh.*, 1912, **33**, 821), who in a similar reaction with *o*-chloronitrobenzene used absolute alcohol and copper powder, both of which have now been found unnecessary].

*3-Chloro-6-nitrodimethylaniline* crystallises from light petroleum in short, stout, dull yellow prisms, often almost cubes, m. p. 49° (Found: Cl, 17.5; *M*, cryoscopic in phenol, 185.9, 187.8; *M*, cryoscopic in naphthalene, 199.5, 210.5.  $C_8H_9O_2N_2Cl$  requires Cl, 17.7%; *M*, 188.5), which are fairly readily volatile in steam. The constitution of this compound was confirmed by its preparation (as above) from 4-chloro-2-bromo- and also from 4-chloro-2-iodonitrobenzene. The *picrate*, prepared from the compound (0.6 g.) and picric acid (0.7 g.) in boiling alcohol (7 c.c.), is deposited, on cooling, in bright yellow, flat prisms, m. p. 70° (Found: Cl, 8.1.  $C_8H_9O_2N_2Cl \cdot C_6H_3O_7N_3$  requires Cl, 8.3%).

*3-Bromo-6-nitrodimethylaniline* separates from light petroleum in crystals, m. p. 58.5°, resembling those of the chloro-analogue (Found: Br, 32.4.  $C_8H_9O_2N_2Br$  requires Br, 32.6%). The *picrate* melts at 85° (Found: Br, 16.6.  $C_8H_9O_2N_2Br \cdot C_6H_3O_7N_3$  requires Br, 16.9%). Their constitutions follow from their identity (mixed m. p., etc.) with the compound and its *picrate* made from 2-chloro-4-bromonitrobenzene by the general process above. The 2-chloro-4-bromonitrobenzene was obtained from 3-chloro-4-nitroaniline by means of the Sandmeyer reaction.

*3-Iodo-6-nitrodimethylaniline* crystallises from light petroleum in long orange prisms, m. p. 52° (Found: I, 43.7.  $C_8H_9O_2N_2I$  requires I, 43.5%). It was also obtained from 2-chloro-4-iodonitrobenzene, prepared from 3-chloro-4-nitroaniline by the usual iodination process. The *picrate* melts at 104° (Found: I, 24.2.  $C_8H_9O_2N_2I \cdot C_6H_3O_7N_3$  requires I, 24.4%). All the 3-halogeno-6-nitrodimethylanilines are precipitated on dilution of their colourless solutions in concentrated sulphuric acid. *o-Nitrodimethylaniline picrate* crystallises from alcohol in long yellow prisms, m. p. 103° (Found: N, 18.0.  $C_8H_{10}O_2N_2 \cdot C_6H_3O_7N_3$  requires N, 17.7%).

*Reduction of the 3-Halogeno-6-nitro- to the 3-Halogeno-6-amino-dimethylanilines.*—Each of the above nitro-compounds is readily



reduced by iron powder and 50% aqueous acetic acid to the corresponding amine, which is then removed by steam distillation from the reaction mixture, made alkaline. The amines are colourless viscous oils of a not unpleasant odour and are volatile in steam. The chloro- and bromo-compounds are conveniently isolated from the steam distillates directly as hydrochlorides, but the iodo-compound, on account of its ready decomposition when boiled with hydrochloric acid, is extracted with ether prior to its conversion into the hydrochloride.

**3-Chloro-6-aminodimethylaniline** (Found: Cl, 20.6.  $C_8H_{11}N_2Cl$  requires Cl, 20.8%) forms a *monohydrochloride*, which crystallises from water in long needles (Found: Cl, 34.1.  $C_8H_{11}N_2Cl.HCl$  requires Cl, 34.3%). The *dihydrochloride* separates from concentrated hydrochloric acid solution in colourless prisms (Found: ionisable Cl, 29.1; total Cl, 43.5.  $C_8H_{11}N_2Cl.2HCl$  requires ionisable Cl, 29.1; total Cl, 43.7%). The *picrate* separates from a hot alcoholic solution of equimolecular quantities of the amine and picric acid in bright yellow prisms, m. p.  $151^\circ$  (to a brown-red liquid) (Found: Cl, 8.7.  $C_8H_{11}N_2Cl.C_6H_3O_7N_3$  requires Cl, 8.9%).

**3-Bromo-6-aminodimethylaniline** (Found: Br, 37.0.  $C_8H_{11}N_2Br$  requires Br, 37.2%) forms a *monohydrochloride* (Found: Cl, 14.1.  $C_8H_{11}N_2Br.HCl$  requires Cl, 14.1%) and a *dihydrochloride* (Found: Cl, 24.6.  $C_8H_{11}N_2Br.2HCl$  requires Cl, 24.6%). The *picrate* crystallises from alcohol in bright yellow prisms, m. p.  $137^\circ$  (Found: Br, 17.9.  $C_8H_{11}N_2Br.C_6H_3O_7N_3$  requires Br, 18.0%).

**3-Iodo-6-aminodimethylaniline** (Found: I, 48.2.  $C_8H_{11}N_2I$  requires I, 48.5%) forms a *monohydrochloride* (Found: Cl, 11.8.  $C_8H_{11}N_2I.HCl$  requires Cl, 11.9%) and a *dihydrochloride* (Found: Cl, 20.0.  $C_8H_{11}N_2I.2HCl$  requires Cl, 21.2%). The latter analysis indicates the presence of monohydrochloride (compare the theoretical discussion). The *picrate* crystallises in thin, bright yellow plates, m. p.  $167^\circ$  (Found: I, 25.6.  $C_8H_{11}N_2I.C_6H_3O_7N_3$  requires I, 25.9%).

**o-Aminodimethylaniline** is prepared as above by reduction of o-nitrodimethylaniline and has b. p.  $212^\circ$  (Found: N, 20.7.  $C_8H_{12}N_2$  requires N, 20.6%). Its *monohydrochloride* separates from concentrated hydrochloric acid in long colourless prisms (Found: Cl, 20.9.  $C_8H_{12}N_2.HCl$  requires Cl, 20.6%). The *picrate* crystallises in bright yellow prisms, m. p.  $136^\circ$  (Found: N, 19.3.  $C_8H_{12}N_2.C_6H_3O_7N_3$  requires N, 19.2%).

The authors desire to thank the British Dyestuffs Corporation for generous gifts of chemicals.

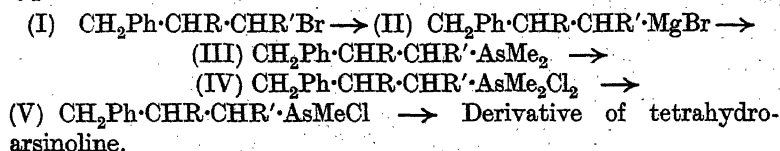
TECHNICAL COLLEGE, HUDDERSFIELD. [Received, December 23rd, 1929.]

# LXX.— $\gamma$ -Phenyl- $\alpha$ -methylpropyldimethylarsine, $\beta$ -Benzylbutyldimethylarsine, and Some Related Compounds.

By ALBERT BREWIN and EUSTACE EBENEZER TURNER.

BEFORE the appearance of the paper by Mills, Parkin, and Ward (J., 1927, 2613), we were attempting to prepare certain derivatives of dihydroarsindole and of tetrahydroarsinoline in which *cis-trans* isomerism should be exhibited. For one reason or another, no suitable ring arsines were obtained, but the results now recorded may be of value to future workers.

We have endeavoured to carry out a number of syntheses of the type :



$\beta$ -Benzylbutyl bromide (I; R = Et, R' = H) readily formed a Grignard reagent, but this reacted with dimethyliodoarsine to give only a poor yield of  $\beta$ -benzylbutyldimethylarsine (as III).

Neither  $\alpha\gamma$ -diphenylpropyl bromide (I; R = H, R' = Ph) nor  $\gamma$ -phenyl- $\alpha$ -m-chlorophenylpropyl bromide (I; R = H, R' = *m*-C<sub>6</sub>H<sub>4</sub>Cl) could be caused to combine with magnesium. On the other hand,  $\gamma$ -bromobutylbenzene readily formed a Grignard reagent, which reacted with dimethyliodoarsine to give  $\gamma$ -phenyl- $\alpha$ -methylpropyldimethylarsine, CH<sub>2</sub>Ph·CH<sub>2</sub>·CHMe·AsMe<sub>2</sub>. The dichloride (as IV) of this substance, however, underwent the expected loss of methyl chloride (on heating) only to the extent of a few units %, the major portion decomposing to give  $\gamma$ -chlorobutylbenzene and dimethylchloroarsine.

## EXPERIMENTAL.

$\beta$ -Benzylbutyl bromide, b. p. 135°/20 mm. (yield, 73%) (Found: Br, 34.9. C<sub>11</sub>H<sub>15</sub>Br requires Br, 35.2%), was prepared from  $\beta$ -benzylbutyl alcohol by means of phosphorus tribromide, the alcohol (b. p. 128—132°/11 mm.) being obtained in 73% yield by reducing ethyl  $\alpha$ -benzylbutyrate (b. p. 133—136°/15 mm.; 145—150°/20 mm.; 155—160°/30 mm.) with sodium and absolute alcohol. The most convenient synthesis of the ester proved to be the following: Benzylidenemalonic acid was prepared (43% yield) and reduced (yield, almost quantitative) by the methods of Claisen and

Crismer (*Annalen*, 1883, **218**, 135). Esterification of the benzylmalonic acid with alcohol and concentrated sulphuric acid proceeded to the extent of 75%, and the resulting ester (b. p.  $170^{\circ}/13$  mm.) gave rise by normal procedure to a 90% yield of ethyl benzylethylmalonate. This was converted by Mohr's method (*J. pr. Chem.*, 1905, **71**, 331) into  $\alpha$ -benzylbutyric acid, b. p.  $175$ — $177^{\circ}/20$  mm. (yield, 77%).

$\beta$ -Benzylbutyldimethylarsine.—A solution of  $\beta$ -benzylbutyl bromide in three times its weight of ether was added gradually to slightly less than one atomic proportion of magnesium turnings, covered with ether, initial interaction being promoted by the use of iodine. Dimethyliodoarsine (1 mol.), dissolved in twice its volume of benzene, was slowly added to the formed Grignard reagent and the whole was gently boiled for an hour. Water and dilute hydrochloric acid were then added and the ether-benzene layer was worked up in the usual manner. The arsine, distilled in a current of hydrogen, was a colourless, strongly smelling oil, b. p.  $150^{\circ}/20$  mm. (yield, 30%).

$\alpha\gamma$ -Diphenylpropyl bromide, b. p.  $185$ — $190^{\circ}/30$  mm. (Found: Br, 29.0.  $C_{15}H_{15}Br$  requires Br, 29.1%), was prepared by the action of phosphorus tribromide on the corresponding alcohol, which was obtained (80 g.) from benzaldehyde and the Grignard reagent from 100 g. of  $\beta$ -phenylethyl bromide.

$\gamma$ -Bromobutylbenzene.— $\beta$ -Phenylethyl bromide (170 g.) was converted into a Grignard reagent, and the latter was treated with 120% of the calculated quantity of acetaldehyde, dissolved in ether. An 85% yield of  $\beta$ -phenylethylmethylcarbinol, b. p.  $124$ — $126^{\circ}/15$  mm., or  $128$ — $130^{\circ}/20$  mm., was obtained, together with a small quantity of  $\alpha\delta$ -diphenylbutane. From 80 g. of the carbinol, by means of phosphorus tribromide, 90 g. of  $\gamma$ -bromobutylbenzene, b. p.  $118$ — $119^{\circ}/14$  mm.,  $129$ — $130^{\circ}/20$  mm., or  $137$ — $138^{\circ}/34$  mm., were obtained (Found: Br, 36.9.  $C_{10}H_{13}Br$  requires Br, 37.5%).

$\gamma$ -Phenyl- $\alpha$ -methylpropyldimethylarsine was obtained in 56% yield from the interaction of dimethyliodoarsine and a Grignard reagent from  $\gamma$ -bromobutylbenzene. It is a colourless, highly refractive oil, b. p.  $143$ — $145^{\circ}/20$  mm., or  $163^{\circ}/50$  mm. The methiodide was readily produced, and formed globular crystals, m. p.  $156^{\circ}$  (softening at  $153^{\circ}$ ) (Found: I, 33.3.  $C_{13}H_{22}IA$ s requires I, 33.5%).

$\gamma$ -Phenyl- $\alpha$ -m-chlorophenylpropyl alcohol was obtained in 64% yield from *m*-chlorobenzaldehyde and magnesium  $\beta$ -phenylethyl bromide in ethereal solution. It boiled at  $210$ — $215^{\circ}/25$  mm. (Found: Cl, 14.65.  $C_{15}H_{15}OCl$  requires Cl, 14.45%).

$\gamma$ -Phenyl- $\alpha$ -m-chlorophenylpropyl bromide was obtained from the alcohol in 43% yield, and boiled at  $200$ — $205^{\circ}/30$  mm. (0.2258 g.

gave 0.2457 g. of  $\text{AgCl} + \text{AgBr}$ .  $\text{C}_{15}\text{H}_{14}\text{ClBr}$  requires 0.2435 g. of  $\text{AgCl} + \text{AgBr}$ .

One of us (A. B.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant held while this investigation was in progress.

EAST LONDON COLLEGE,  
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## LXXI.—*The Reactivity of Halogen Atoms in Compounds of the Pyridine Series. Part I. The Halides of 2-Stilbazole.*

By JOHN WALTER BLOOD and BRIAN DUNCAN SHAW.

BAURATH (*Ber.*, 1887, **20**, 2719; 1888, **21**, 818) found that 2-stilbazole (2-styrylpyridine) dibromide reacted with alcoholic potassium hydroxide, but was unable to isolate an acetylenic base analogous to tolane. Ladenburg (*Ber.*, 1903, **36**, 119), who reinvestigated the reaction at higher temperatures, described his product as deoxybenzazoin. Five years ago, one of us observed that the action of pyridine upon the dibromide regenerated 2-stilbazole. This evidence of the presence of a "positive" bromine atom led us to study the reaction of a variety of other reagents. Pyridine, phenol, aqueous-alcoholic potassium hydroxide, potassium iodide, and hydriodic acid yield 2-stilbazole even when the quantity of reagent is equivalent only to one bromine atom; indicating that after replacement of one bromine atom with hydrogen, loss of hydrogen bromide occurs spontaneously. This agrees with the known inability of 2-stilbazole to combine additively with hydrogen bromide at the ethylenic linking (compare Rath, *Ber.*, 1924, **57**, 841). On the other hand, with piperidine or sodium ethoxide a *monobromostilbazole* results, and alcoholic potassium hydroxide containing very little water yields a mixture of stilbazole and bromostilbazole. The position of the bromine atom in the latter compound, which is singularly unreactive, has not yet been determined; but as one of us has been obliged to abandon the work, the results so far obtained are now given. Similar results were obtained with 2-stilbazole *dichloride*. When stilbazole was the product, a small quantity of oil usually accompanied the solid base. This oil gradually yielded the solid base and treatment with bromine gave stilbazole dibromide. Similar oils accompanied the solid chloro- and bromo-stilbazoles; these also solidified on long standing. The investigation is being extended to the isomeric stilbazoles and their substitution products.

## EXPERIMENTAL.

*The 2-Stilbazole Chlorides.*—A solution of chlorine (7.1 g.; 1 mol.) in carbon tetrachloride (50 c.c.) was added gradually to a solution of 2-stilbazole (18.1 g.; 1 mol.) in the same solvent. The mixture boiled, and was cooled in water; a gummy solid then separated. The clear solution deposited colourless needles of 2-stilbazole dichloride, m. p. 153—154° after recrystallisation from alcohol. The dichloride was readily soluble in acetone and sparingly soluble in cold alcohol, chloroform, or carbon tetrachloride (Found: Cl, 28.3.  $C_{13}H_{11}NCl_2$  requires Cl, 28.2%). A little unchanged stilbazole was recovered from the mother-liquor.

The gummy solid was dissolved in hot alcohol; on cooling, small plates of 2-stilbazole tetrachloride were deposited, m. p. 180—181° after recrystallisation from alcohol (Found: Cl, 43.6.  $C_{13}H_{11}NCl_4$  requires Cl, 43.96%). On treatment with cold aqueous sodium carbonate solution the compound readily gave the dichloride, indicating that half the chlorine was united to the nitrogen atom.

*The 2-Stilbazole Bromides.*—In the preparation of the dibromide by Baurath's method (*loc. cit.*) it was found better to employ less than the theoretical amount of bromine, as otherwise the product was contaminated with a yellow insoluble substance which appeared to be 2-stilbazole tetrabromide. The compound decomposed on being heated. Consistent analytical results could not be obtained, as it gradually lost bromine on exposure to the atmosphere, yielding the dibromide. The latter, crystallised from alcohol, had m. p. 172° (Baurath gives 166—167°).

*Action of Reagents upon the Stilbazole Dihalides.*—Except where otherwise stated, the results with the dichloride were exactly similar to those given for the dibromide.

*Alcoholic potassium hydroxide.* 2-Stilbazole dibromide (6.8 g.; 1 mol.) was boiled with a solution of potassium hydroxide (2.28 g.; 2 mols.) in 95% alcohol (50 c.c.). The solution rapidly became red, but was still alkaline after 6 hours. The alcohol was removed, water added to the residue, and the brown oil extracted with benzene. After removal of the solvent the oil was treated with successive small quantities of light petroleum (b. p. 50—60°). The first fractions deposited long, pale yellow prisms of monobromostilbazole, which were obtained colourless by recrystallisation from alcohol; m. p. 74—75° (Found: C, 60.15; H, 4.0; Br, 30.5.  $C_{13}H_{10}NBr$  requires C, 60.2; H, 3.9; Br, 30.8%).

The later light petroleum fractions were coloured, and left a thick brown oil on removal of the solvent. The residue was distilled with steam; a colourless oil, which distilled very slowly, was separated with benzene. After removal of the solvent the pale

brown oil partly crystallised. The solid, after crystallisation from light petroleum, had m. p.  $91^{\circ}$  alone or mixed with 2-stilbazole. A portion of the residual oil gave, with bromine, 2-stilbazole dibromide, m. p.  $172^{\circ}$ . The remainder, on exposure to the air, yielded the solid base. Yields: bromostilbazole 1.5 g., 2-stilbazole 2.1 g.; 30% and 60% of the theoretical respectively. Increase in the percentage of water raised the proportion of 2-stilbazole.

In a repetition experiment the mixture was not heated, but kept at room temperature for 2 days. Yields: bromostilbazole 2.5 g., 2-stilbazole 0.32 g.; 50% and 9% of the theoretical respectively. The residual oil slowly deposited more of the solid bromostilbazole.

*Sodium ethoxide.* Preparation of monobromostilbazole. A solution of sodium (0.35 g.; 1 atom) in anhydrous alcohol (7.0 c.c.) was added to stilbazole dibromide (5.1 g.; 1 mol.). A reaction commenced on warming and was complete after 5 minutes' boiling. Water (50 c.c.) precipitated an oil which solidified when rubbed; yield, 3.8 g. (85% of the theoretical). Crystallisation from light petroleum gave long colourless prisms, m. p.  $75^{\circ}$ . The mother-liquor, after evaporation, left an oil which gave solid monobromostilbazole on long standing. The length of the crystals obtained by slow crystallisation from light petroleum appears to be limited only by the size of the vessel. From alcohol, on the other hand, large compact prisms are obtained.

*Pyridine.* 2-Stilbazole dibromide (3.4 g.) was boiled with pyridine (6 g.) for 1 hour. The dark solution was poured into water, and the solid crystallised from alcohol; m. p.  $90-91^{\circ}$ , mixed m. p. (with 2-stilbazole)  $90-91^{\circ}$ . Yield, 1.35 g. (75% of the theoretical).

*Piperidine.* 2-Stilbazole dibromide (6.8 g.) was heated on the water-bath with piperidine (5 g.) during 10 minutes. The semi-solid product was treated with water (30 c.c.) and extracted with benzene. The solvent was removed and the residual oil crystallised from light petroleum; m. p.  $74-75^{\circ}$ ; yield, 3.3 g. of monobromostilbazole (63% of the theoretical). A small quantity of oil was not examined.

*Potassium iodide.* 2-Stilbazole dibromide (0.2049 g.) was boiled with potassium iodide (4 g.) in alcoholic solution (100 c.c.). The reaction was followed by titration of aliquot portions of the liquid, largely diluted with water, with *N*/10-sodium thiosulphate solution. After 3 hours, the rate of liberation of iodine slackened and became constant; total, 0.1820 g.  $I_2$ . In a parallel experiment from which the dibromide was omitted, 0.025 g.  $I_2$  was liberated; difference 0.1570 g. Theoretical, calculated from the equation  $C_5NH_4 \cdot CHBr \cdot CHBrPh + 2KI = C_5NH_4 \cdot CH \cdot CHPh + 2KBr + I_2$ , 0.1527 g.

*Hydriodic acid.* 2-Stilbazole dibromide (0.110 g.) was heated on the

water-bath with potassium iodide (0.10 g.) in acetic acid (10 g.). The iodine liberated was titrated with *N*/10-sodium thiosulphate solution. Found, 0.080 g. The equation  $C_5NH_4 \cdot CHBr \cdot CHBrPh + 2HI = C_5NH_4 \cdot CH \cdot CHPh + 2HBr + I_2$  requires 0.0804 g.

A mixture of 2-stilbazole dibromide (3.4 g.; 1 mol.), acetic acid (10 c.c.), and potassium iodide (3.34 g.; 2 mols.) was heated to boiling and rapidly cooled to 15°. The brown crystalline mass which separated was removed, pressed, and treated with sulphurous acid to remove iodine. The yellow needles obtained softened at 96°, melted at 100°, resolidified at 116–120°, and again melted at 179–180°. A portion crystallised from hot water and dried at 100° had m. p. 182–184°, and mixed m. p. (with an authentic specimen of 2-stilbazole hydriodide) 182–184° (Found: *I*, 36.6; *M*, by titration with *N*/10-NaOH, 341. Calc. for  $C_{13}H_{11}N, HI, 2H_2O$ : *I*, 36.8%; *M*, 345). A portion gave with sodium carbonate solution a white solid, m. p. 90–91°; mixed m. p. (with 2-stilbazole) 90–91°.

*Phenol.* 2-Stilbazole dibromide (2.5 g.) was heated with phenol (0.50 g.; excess) at the melting point of the mixture during 2 hours. The solid product was dissolved in hot alcohol; needles of hydrated 2-stilbazole hydrobromide, m. p. 187–189°, separated on cooling. Treatment with sodium carbonate gave 2-stilbazole, m. p. 90–91°. The alcoholic mother-liquor was poured into water; the red solid obtained, crystallised from hot water, had m. p. 94–95°, and mixed m. p. (with tribromophenol) 94–95°.

An authentic specimen of 2-stilbazole hydrobromide was prepared from the pure base in needles, readily soluble in hot water and sparingly soluble in alcohol; m. p. (anhydrous) 188–189° (Found: *M*, 280.5.  $C_{13}H_{11}N, HBr, H_2O$  requires *M*, 280).

The experiment was repeated, sufficient phenol being used to remove only half the bromine as tribromophenol; the result was as before.

*Action of Sodium Ethoxide upon 2-Stilbazole Dichloride.*—To a solution of sodium (0.50 g.) in anhydrous alcohol (10 c.c.), 2-stilbazole dichloride (3 g.) was added, and the solution boiled during 10 minutes. The alcohol was removed, the residue treated with water and extracted with benzene, the solvent removed, and the oil dissolved in light petroleum; colourless prisms of monochlorostilbazole, m. p. 63°, readily soluble in alcohol and sparingly soluble in light petroleum, were obtained (Found: *Cl*, 16.5.  $C_{13}H_{10}NCl$  requires *Cl*, 16.4%).

The authors are indebted to Professor F. S. Kipping, F.R.S., for his interest in this work, and to the South Metropolitan Gas Company for a supply of pyridine bases.

LXXII.—*Digoxin, a New Digitalis Glucoside.*

By SYDNEY SMITH.

IN recent years it has been shown that the leaves of *Digitalis lanata* have a greater physiological activity than those of *Digitalis purpurea*, the species used in medicine; e.g., Wokes (*Quart. J. Pharm. Pharmacol.*, 1929, 2, 292) found the potency of a specimen of *Digitalis lanata* to be 3.5—4 times that of the international standard leaf.

The total glucosides of the leaves of this species were therefore isolated and fractionated in order to separate the glucosides and compare them with those from the official species. This part of the work is not yet completed, but during the fractionation a glucoside was obtained in small amount differing from those hitherto known. This new glucoside, which has been named *digoxin*, resembles gitoxin in its sparing solubility in chloroform, but is readily distinguished from it by giving an olive-brown colour completely free from red when dissolved in acetic acid containing a trace of ferric chloride and treated with sulphuric acid (Keller reaction). In the latter respect it is similar to pure digitoxin. Digoxin is optically active. It is very easily hydrolysed and gives a crystalline genin and only one sugar, digitoxose. The results of combustion and the molecular-weight determinations of the genin suggest the empirical formulæ  $C_{41}H_{64}O_{14}$  and  $C_{23}H_{34}O_5$  for digoxin and *digoxigenin* respectively and the yields of the hydrolytic products are in agreement with the equation  $C_{41}H_{64}O_{14} + 3H_2O = C_{23}H_{34}O_5 + 3C_6H_{12}O_4$ .

Dr. J. W. Trevan, of the Wellcome Physiological Research Laboratories, has kindly estimated the activity of the glucoside and its genin by the Trevan and Boock frog method with the following results: 1 mg. of digoxin is equivalent to 0.28 mg. of standard ouabain and 1 mg. of digoxigenin is equivalent to 0.026 mg. of standard ouabain.

## EXPERIMENTAL.

The total glucosides were dissolved in acetone and kept for some time until a mixture of the less soluble glucosides (fraction A) separated. The mother-liquor was diluted with water and allowed to stand. The precipitate (fraction B) was separated, and the filtrate saturated with sodium chloride (fraction C). Each of these three precipitates contained digoxin. The acetone crop (A) may be worked up by dissolving it in 80% alcohol and concentrating the solution under diminished pressure until solid separates; after filtering, the solution is concentrated and one or two further crops are obtained. By boiling each fraction with chloroform or ethyl acetate,



a sparingly soluble portion is obtained which is purified by solution in 80% alcohol and concentration as before. The purification is continued in this way until the specific rotation remains unchanged and the Keller reaction gives an olive-brown colour completely free from any trace of red. Fractions B and C may be worked up by dissolving them in alcohol and gradually diluting the solutions with water. The less soluble fractions are then purified by the process described for fraction A.

*Digoxin* crystallises from dilute alcohol or from pyridine and water in colourless, four- or five-sided plates free from solvent (Found in material dried at 100° in a vacuum: C, 63.1, 63.1, 63.0; H, 8.2, 8.3, 8.2.  $C_{41}H_{64}O_{14}$  requires C, 63.0; H, 8.3%). The m. p. varies with the rate of heating, but when placed in a bath at 260° and slowly heated, the substance melts and decomposes at about 265° (corr.). It is almost insoluble in chloroform, ethyl acetate, and acetone, but dissolves in a mixture of chloroform and alcohol or in pyridine or dilute alcohol. It is more soluble in hot 80% alcohol than gitoxin. In pyridine solution the specific rotation  $[\alpha]_{5461}^{20} = +13.3^\circ$  ( $c = 1.5$ ). Like digitoxin and gitoxin, digoxin gives on heating an oily distillate which readily crystallises.

*Hydrolysis of digoxin.* Digoxin (2.903 g. dried at 100° in a vacuum) was boiled under reflux with a mixture of alcohol (290 c.c.) and water (290 c.c.) containing 2.25 c.c. of hydrochloric acid ( $d$  1.16) for  $\frac{1}{2}$  hour. The solution was neutralised with sodium hydroxide and concentrated under reduced pressure. The genin separated in well-defined prisms and after drying at 80° in a vacuum weighed 1.387 g. (47.8%). The filtrate and washings were diluted to 200 c.c. and after addition of 0.4 c.c. of concentrated hydrochloric acid the mixture was heated on a water-bath for 20 minutes. After cooling, the liquid was extracted with chloroform, which removed a trace of sticky material (0.037 g.; 1.3%). The aqueous liquid was neutralised with sodium hydroxide and evaporated to dryness under diminished pressure, the residue was thoroughly dried over sulphuric acid in a vacuum desiccator and extracted with dry acetone, and the extract was evaporated to dryness. The residual sugar rapidly crystallised and after drying at 80° in a vacuum weighed 1.541 g. (53.1%).

*Digoxigenin.* The anhydrous genin without purification had  $[\alpha]_{5461}^{20} = +25.8^\circ$  ( $c$  in methyl alcohol, 1.04). After one crystallisation from ethyl acetate it had  $[\alpha]_{5461}^{20} + 27.0^\circ$  ( $c$  in methyl alcohol, 1.77), and this value was not altered by further crystallisation. *Digoxigenin* separates from ethyl acetate in stout colourless prisms free from solvent, m. p. 222° (corr.). It crystallises from dilute alcohol in prismatic rods containing water of crystallisation. When dissolved

in glacial acetic acid containing a trace of ferric chloride and treated with sulphuric acid, it gives a greenish-yellow ring (Found for the air-dried crystals: C, 64.5; H, 8.8; loss at 80° in a vacuum, 8.6.  $C_{23}H_{34}O_5 \cdot 2H_2O$  requires C, 64.7; H, 9.0;  $H_2O$ , 8.5%. Found for the substance dried in a vacuum at 80°: C, 70.7, 70.5, 70.7, 70.4; H, 8.6, 8.6, 8.7, 8.7; *M*, in camphor, 394, 366, 372.  $C_{23}H_{34}O_5$  requires C, 70.7; H, 8.8%; *M*, 390.3).

*Digitoxose*. The sugar (1.541 g.) without purification had  $[\alpha]_{5461}^{20} + 55.5^\circ$  (*c* in water, 1.6). After crystallisation from ethyl acetate it had  $[\alpha]_{5461}^{20} + 55.6^\circ$  and melted at 104°. Yield of successive crops, 1.134 g., 0.145 g., and 0.084 g. (total, 88.5%). By recrystallisation the *m. p.* was raised to 112°. Cloetta (*Arch. Exp. Path. Pharm.*, 1926, 112, 276) recorded 110°. The sugar gave the Keller reaction characteristic of digitoxose (Found: C, 48.9, 48.6; H, 8.2, 8.2. Calc. for  $C_6H_{12}O_4$ : C, 48.6; H, 8.2%).

The author is indebted to Dr. Hill, Director of the Royal Botanic Gardens, Kew, for the botanical verification of the material used and to Mr. A. Bennett for the micro-analyses.

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### LXXIII.—*Properties of Conjugated Compounds. Part VIII. Addition of Bromine to $\alpha\delta$ -, $\alpha\gamma$ -, and $\beta\gamma$ -Dimethylbutadienes.*

By ERNEST HAROLD FARMER, CYRIL DUNN LAWRENCE, and WILLIAM DALLAS SCOTT.

THE experiments here described are a continuation of the investigation on the influence of substitution in the butadiene chain on (1) the tendency towards the initial formation of adjacent and terminal dibromides and (2) the related structural mobility of the dibromides themselves. As in previous papers, all methods of determining the constitutions of the bromination products which involve the formation and decomposition of cyclic oxides, interactions with sodiomalonic esters, amines, etc., have been rejected; reliance has been placed on the detailed examination of the action of permanganate and of ozone, and densities and refractive indices have frequently been determined as an aid in detecting isomerisation. The conclusions reached for each hydrocarbon are based on the observations made over a large number of bromination and oxidation experiments.

*$\alpha\delta$ -Dimethylbutadiene.*—The addition of bromine to  $\alpha\delta$ -dimethylbutadiene has been examined by Duden and Lemme (*Ber.*, 1902, **35**, 1338), who obtained their hydrocarbon by the removal of hydrogen bromide from  $\beta\epsilon$ -dibromohexane with quinoline. The boiling point of their specimen was somewhat high ( $87$ – $89^\circ$ ),\* but evidence was brought forward which showed that the major portion of the (distilled) dibromide obtained therefrom was the terminal dibromide.

Our experiments have shown that the dibromide produced is a stable compound having no recognisable tendency towards isomerisation at room temperature or on heating. The densities and refractive indices of freshly prepared, distilled, and aged specimens are identical, and the evidence of oxidation processes indicates the absence therefrom of any proportion of an isomeride. Consequently the formation of a homogeneous terminal dibromide from this hydrocarbon appears to be more complete than in any instance yet investigated. In order to show this directly, attempts have been made to convert the dibromide quantitatively into its dihydroxy-derivative,  $\text{CHMeBr}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CHMeBr}$ , a solid form of which (see p. 516) is readily produced during oxidation with permanganate. Invariably, however, two dibromoglycols are formed—the solid already mentioned (representing about 60% of the dibromide which suffers oxidation) and a liquid which loses hydrogen bromide during distillation. The former resists the further action of cold permanganate, but the latter is so readily attacked that its degradation proceeds side by side with the preliminary hydroxylation of the hydrocarbon dibromide. Consequently the liquid dibromoglycol is always accompanied by considerable quantities of  $\alpha$ -bromopropionic, lactic, and pyruvic acids: presumably these are its own degradation products, but since it is obtainable only in small yield, a direct demonstration of its oxidisability to these substances has not been possible.

*$\alpha\gamma$ -Dimethylbutadiene.*—The hydrocarbon was obtained by dehydration of  $\beta$ -methylpentane- $\beta\delta$ -diol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ , the reduction product of diacetone alcohol. Our early experiments on the oxidation of the derived dibromide at once showed that the constitution of  $\alpha\alpha$ -dimethylbutadiene assigned to the hydrocarbon by Kyriakides (*J. Amer. Chem. Soc.*, 1914, **36**, 994) was incorrect.

\* The homogeneity of conjugated hydrocarbons prepared by recorded methods has been concurrently investigated by one of us with Dr. F. L. Warren. The results of this investigation will shortly be published together with the physical properties of the seven mono- and di-methylbutadienes. For this reason, physical data (other than boiling points) relating to hydrocarbons are here omitted. For convenience in this and subsequent papers, the Geneva names for the hydrocarbons are restricted to the experimental portion.

but details of the establishment of the alternative constitution are here omitted because Diels and Alder (*Annalen*, 1929, 470, 98) have shown that this and several other methods believed to give the  $\alpha\alpha$ -hydrocarbon yield in fact the  $\alpha\gamma$ -isomeride. The intermediate dehydration product, represented as  $\text{CMe}_2\cdot\text{CH}\cdot\text{CHMe}\cdot\text{OH}$  by Kyriakides, is probably an isomeric methylpentenol, since we could not isolate acetone from its oxidation products.

The oily dibromide obtained from  $\alpha\gamma$ -dimethylbutadiene is unstable, suffering partial degradation to a monobromide on heating or (slowly) on standing. Since at *each* successive distillation a considerable portion of the dibromide is broken down, leaving a residue which is to all appearances homogeneous and without tendency towards isomeric change, there is nothing to suggest that a preferential degradation of one component in a mixture of  $\alpha\beta$ - (or  $\gamma\delta$ -) and  $\alpha\delta$ -dibromides is taking place. The densities of freshly prepared undistilled and distilled samples do indeed differ slightly (1.586 and 1.603 respectively), probably owing to the formation of a trace of monobromide during the isolation of the former. Permanganate oxidation experiments with distilled and undistilled specimens of the dibromide show that *at least* it consists largely of the terminally dibrominated compound  $\text{CHMeBr}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2\text{Br}$ , and both permanganate and ozone oxidations fail to furnish any vestige of positive evidence pointing to the initial occurrence of a proportion of an  $\alpha\beta$ - or  $\gamma\delta$ -isomeride. Although ozonolysis might be expected to reveal the presence of any appreciable proportion of either of these forms, the difficulties attending the examination of the products of permanganate oxidation and of ozonolysis are such that small quantities of their degradation products could remain undetected. Permanganate oxidation follows a course similar to that outlined in the preceding section, and therefore quantitative conversion into stereoisomeric dibromoglycols is not possible.

*$\beta\gamma$ -Dimethylbutadiene.*—The bromination of  $\beta\gamma$ -dimethylbutadiene has been extensively investigated (Mariuza, *J. Russ. Phys. Chem. Soc.*, 1889, 21, 434; Couturier, *Ann. Chim.*, 1892, 26, 480; Kondakov, *J. pr. Chem.*, 1900, 62, 166; Courtot, *Bull. Soc. chim.*, 1906, 35, 969). The completion of our study of this process synchronised with the publication of further work on the subject by Macallum and Whitby (*Trans. Roy. Soc. Canada*, 1928, III, 22, 33), to whom we are indebted for an early copy of their memoir.

*$\beta\gamma$ -Dimethylbutadiene*, when brominated at a low temperature, readily yields a mixture of dibromides. The main constituent is a solid terminal dibromide,  $\text{CH}_2\text{Br}\cdot\text{CMe}\cdot\text{CMe}\cdot\text{CH}_2\text{Br}$ , m. p.  $47^\circ$  (Kondakov, *loc. cit.*; Macallum and Whitby, *loc. cit.*; p. 520 below), but the nature of the residual liquid product has not been determined.

Assuming that the liquid, like the solid, is an  $\alpha\delta$ -compound, Macallum and Whitby attempted to determine which is the *cis*- and which the *trans*-form by causing reaction with diethylamine. The results were anomalous and the authors state that the explanation may be that the liquid dibromide is a mixture rather than a chemical individual.

The liquid dibromide cannot be freed from the dissolved solid form by repeated freezing and filtration (with or without a solvent); the freezing point of the residual liquid, however, rises considerably and the density diminishes. A close estimate of the composition of the dibromide mixture has consequently not been possible. The solid form is certainly produced originally to the extent of more than 80% of the total yield, and it gives, on heating at 100°, a liquid which is *in no respect distinguishable* (this applies to general properties and behaviour on oxidation and distillation) from that obtained by direct bromination. This liquid, after being freed as far as possible from the solid form, represents about 18% of the bromide taken. The reverse change, liquid  $\rightarrow$  solid, can be brought about by heating for a short time at 100°; we have not thus succeeded in obtaining so high a yield as 80% of the solid form, but estimation has been difficult with the comparatively small quantities of purified material available. The use of quinoline perbromide as a brominating agent causes a considerable diminution in the proportion of solid bromide separable from the product but offers practical difficulties in large-scale preparations.

Macallum and Whitby state that both liquid and solid dibromides distil at 105–110°/18.5 mm. We have found, by repeated tests with the "frozen out" liquid, that distillation begins at 101° and continues to 105° at 15 mm. (the solid distils at 103–105° with some change to the liquid form); the character of the fractions collected over 1° ranges indicates that the solid form (already present or formed during distillation) progressively volatilises in the vapour of the liquid form. Nevertheless, the difference in boiling point of the two substances is much smaller than that of the corresponding butadiene derivatives.

Long-continued degradation experiments have failed to demonstrate that the liquid form is the  $\alpha\beta$ -dibromide. In all our oxidations, as was to be expected, degradation products from the solid dibromide appeared. Otherwise the products from the two dibromides differed considerably. Ozonolysis of  $\alpha\beta$ -hydrocarbon dibromides has rarely been satisfactory in our hands; gross decomposition, involving loss of hydrogen bromide, usually occurs during hydrolysis of the ozonide, and, in this instance, although the presence of formaldehyde and of a bromo-ketone other than bromoacetone could be detected amongst the non-resinous products, the expected

ketone  $\text{CH}_3\text{CO}\cdot\text{CMeBr}\cdot\text{CH}_2\text{Br}$  (or its debromination product, methyl isopropenyl ketone) could not be recognised. Nevertheless, in view of the fact that ozonolysis of the solid dibromide readily gives bromoacetone in more than 80% of the theoretical yield, the difference in behaviour of the two isomerides on oxidation is hardly to be reconciled with a differentiation of merely *cis-trans*-nature. There remains for consideration the possibility that the liquid portion of the bromination product is a mixture of two liquid dibromides, namely, the  $\alpha\beta$ - and the *cis*- $\alpha\delta$ -compound. No adequate ground for considering this to be the case has been encountered, yet statements or suggestions to the effect that the *cis*- $\alpha\delta$ -dibromide is the principal constituent of the bromination product are exceedingly difficult to prove or disprove: it is very doubtful if any constitutional significance is to be attached to the double decomposition reactions (Braun, *Ber.*, 1922, 55, 3536; Macallum and Whitby, *loc. cit.*) of substances so mobile as those under consideration.

In this series of papers, the addition of bromine to hexatriene, butadiene, cyclopentadiene, cyclohexadiene, and three of the five dimethylbutadienes has been discussed. Amongst these instances the isomerising capacity of dibromide forms is widespread: yet with fair certainty in the case of  $\alpha\delta$ -dimethylbutadiene and with a high degree of probability in the case of  $\alpha\gamma$ -dimethylbutadiene it has been shown that the bromination product is entirely non-mobile; moreover, in neither of the latter instances has it been possible in a large number of experiments (free bromine being the addendum) to alter recognisably the composition of the bromination mixture. It seems unlikely, therefore, that experimental conditions leading to the production of only  $\alpha\beta$ - ( $\gamma\delta$ -) forms could be obtained in these instances, and, that being so, the *general* possibility in this direction disappears. Of the hydrocarbons mentioned above, only cyclohexadiene (J., 1929, 172) has been considered to suffer complete  $\alpha\beta$ -dibromination, and in determining the orientation of its dibromides importance has been attached to the great contrast between the oxidisability and extent of degradation of the dibromoglycols from original and from derived forms. It is now clear that there is quite a considerable, although less marked, difference in oxidisability of the isomeric dibromoglycols from  $\alpha\delta$ -forms (the carbon atoms carrying bromine are not here, however, oxidised to carboxyl) and to this extent the evidence formerly relied on is weakened. An attempt is being made to improve the oxidative technique employed in the degradation of dibromoglycols, and it is hoped later to supplement the evidence already brought forward in connexion with the constitution of the cyclohexadiene addition products.

## EXPERIMENTAL.

$\alpha\delta$ -Dimethylbutadiene ( $\Delta^{88}$ -hexadiene) was prepared by the catalytic dehydration of ethylpropenylcarbinol (Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 994). The hydrocarbon, after being thoroughly washed and dried, was fractionated over sodium, the portion of b. p.  $80-82^\circ$  being used. This preparation gave a quantitative yield of 3 : 6-dimethyl- $\Delta^4$ -tetrahydropthalic anhydride, m. p.  $92^\circ$ , with maleic anhydride (Found: C, 66.7; H, 6.65. Calc. for  $C_{10}H_{12}O_3$ : C, 66.7; H, 6.7%). Diels and Alder (*loc. cit.*, p. 102) give the m. p. as  $95-96^\circ$ .

*Bromination.* This was carried out under conditions similar to those previously described (Farmer and Scott, J., 1929, 172). The dibromination product, after removal of the solvent (both hexane and chloroform were used), was an almost colourless oil (Found: Br, 65.8.  $C_6H_{10}Br_2$  requires Br, 66.1%). It had  $d_4^{20}$  1.621 and  $n_D^{20}$  1.536 immediately after isolation, and almost the same values after it had been (a) slowly distilled or (b) kept at room temperature for several days. On distillation the crude dibromide in the different preparations yielded only insignificant quantities of low-boiling material. The distillate was always a colourless oil (b. p.  $85^\circ/11$  mm.,  $d_4^{20}$  1.622,  $n_D^{20}$  1.534. Found: Br, 66.2%) which appeared to be homogeneous (Duden and Lemme, *loc. cit.*, also give b. p.  $85^\circ/11$  mm.). Distilled and undistilled specimens of the substance were repeatedly submitted to oxidation with permanganate and with ozone (see below) in order to detect admixed isomeric dibromides, if such were present. The failure to find even small amounts of the degradation products of the latter, and the complete absence of any detectable tendency to partial isomerisation as revealed by changing physical constants, point to the fact that the addition product is pure  $\beta\epsilon$ -dibromo- $\Delta^7$ -hexene.

Unless the bromination was carried out in very dilute solution, there was a tendency towards the production of tetrabromides.

*Oxidation of  $\beta\epsilon$ -Dibromo- $\Delta^7$ -hexene.*—The oxidation with neutral permanganate at  $0^\circ$  was carried out essentially as previously described (Farmer and Scott, J., 1929, 172). Since no difference could be detected between the oxidation products of distilled and of undistilled specimens of the dibromide, only typical experiments are here included. In these, 20 g. portions of the dibromide, dissolved in acetone, were supplied with (a) 1 atom and (b) 4 atoms of oxygen per molecule.

(a) On removal of the acetone from the filtered oxidation liquor in a current of air, a semi-solid mixture separated containing unchanged dibromide. This was combined with a small residue from the acetone washings of the manganese mud. The solid

portion of the mixture was removed, and the filtrate thoroughly extracted with water; the residue was unchanged dibromide. The aqueous liquor, together with the cold aqueous extract of the manganese mud, yielded, on extraction with pure ether, a syrup from which crystals of the solid material separated. This solid, which crystallised from petroleum in colourless prisms, m. p.  $95^{\circ}$ , was  $\beta$ -dibromohexane- $\gamma$ -diol and was doubtless identical with the dibromohexanediol of Duden and Lemme, for which no m. p. is recorded (Found: Br, 58.0.  $C_6H_{12}O_2Br_2$  requires Br, 58.0%). On further oxidation with permanganate it was converted into  $\alpha$ -bromopropionic acid, mixed with some lactic acid, and finally into pyruvic acid (phenylhydrazone, m. p.  $191^{\circ}$ ; mixed m. p. with authentic specimen,  $191^{\circ}$ ); with aqueous chromic acid it gave a 75% yield of crystalline  $\alpha$ -bromopropionic acid (Found: Br, 52.4; equiv., 153. Calc.: Br, 52.3%; equiv., 153).

The water-soluble syrup accompanying the solid dibromohexanediol, when freed as thoroughly as possible from the latter, amounted to 5–10% of the total oxidation products isolated. Although it differed considerably from the solid dibromoglycol in its greatly inferior stability towards permanganate and towards heat, it appeared to be a stereoisomeride (or mixture of stereoisomerides) of  $\beta$ -dibromohexane- $\gamma$ -diol (Found: Br, 58.4%). When it was heated under reduced pressure, decomposition took place, giving dehydrobromination products which appeared to be partly of cyclic-oxide and partly of ethylenic type (the main portion, b. p.  $115$ – $125^{\circ}/1$  mm., corresponded closely in bromine content to the formula  $C_6H_{11}O_2Br$ ); the highest fraction (about  $1/3$  of the whole), however, consisted of the solid dibromoglycol, which appeared to have been formed by isomerisation during heating. The liquid dibromoglycol was obtained in reasonably pure condition only at a late stage in the experiments and the amount of material accumulated was insufficient for making trustworthy observations as to its oxidation products. The aqueous liquors, when acidified and extracted with ether, yielded a small quantity of acidic liquid. This was fractionated and consisted mainly of  $\alpha$ -bromopropionic acid; pyruvic acid was present in the very small, low-boiling fraction.

(b) In effecting more complete oxidation of distilled and of undistilled specimens of the dibromide it was desired to search for  $\alpha\beta$ -dibromobutyric and  $\alpha$ -bromocrotonic acids, the acidic fission products of an  $\alpha\beta$ -dibromide (acetic acid, the complementary fission product, if detected, could have arisen from the acetone used as solvent). The acid product, when carefully fractionated, was found to consist mainly of  $\alpha$ -bromopropionic acid, mixed with lactic acid



and a little pyruvic acid—this mixture gave excellent yields of pyruvic acid on further oxidation—but  $\alpha\beta$ -dibromobutyric or  $\alpha$ -bromocrotonic acid could not be found.

The absence of any significant quantity of an  $\alpha\beta$ -dibromide followed, however, more convincingly from the result of parallel ozonisation experiments. In all these experiments the decomposition of the ozonide by water was carried out at the lowest effective temperature while carbon dioxide was passed through the apparatus to sweep out any acetaldehyde or other volatile product that might have been formed. Immediately the decomposition was complete the cold aqueous reaction product was treated with 30% hydrogen peroxide and kept for 12 hours (isolation of the brominated products as aldehydes was not possible owing to their facile polymerisation). In no experiment could a trace of acetaldehyde, or indeed any highly volatile product, be detected; similarly, none of the degradation products to be expected from an  $\alpha\beta$ -dibromide could be separated or derived from the acidic reaction product.

*$\alpha\gamma$ -Dimethylbutadiene* (*8-Methyl- $\Delta^{8,9}$ -pentadiene*).—The hydrocarbon (see p. 511), after being thoroughly washed with water and fractionated over sodium, boiled at 75.8–76.0°. It gave a quantitative yield of the maleic anhydride addition compound.

*Bromination.* Both hexane and chloroform were used as solvents during bromine addition, but no difference could be detected in the products. The undistilled dibromide,  $d_4^{20.5}$  1.624, was an almost colourless oil (Found: Br, 66.1.  $C_6H_{10}Br_2$  requires Br, 66.1%).

On distillation the dibromide decomposed to an extent which varied in different experiments. Fractions were collected, as shown below, some carbonised residue always remaining in the flask.

B. p. at 22 mm.	Proportion (%).	Bromine content (%).
70—86°	3—7	52.8
86—96	6—11	61.2
96—104	50—80	66.0
104—115	10—15	—

The bromine content showed that, although more than half the distilled material consisted of dibromide, a considerable portion had lost hydrogen bromide. At each subsequent redistillation of the dibromide fraction (b. p. 101–103°/22 mm.) a partly carbonised residue and a low-boiling fraction (below 80°/22 mm.) were again obtained, the yield of the latter depending to some extent on the rate of distillation. Redistillation of the low-boiling portions yielded a colourless oil, b. p. 60–62°/22 mm., which was apparently an almost pure bromo- $\alpha\delta$ -dimethylbutadiene (Found: Br, 51.1.

$C_6H_9Br$  requires Br, 49.6%). As a result of the observations here recorded, the original dibromination product is regarded as pure or only slightly impure  $\beta\epsilon$ -dibromo- $\delta$ -methyl- $\Delta^8$ -pentene.

*Oxidation of  $\beta\epsilon$ -Dibromo- $\delta$ -methyl- $\Delta^8$ -pentene.*—Here also, repeated experiments disclosed no constitutional difference between freshly prepared, undistilled specimens, and the dibromide fraction of b. p. 101–103°/22 mm.; accordingly, in the following account of oxidation by (a) ozone and (b) neutral permanganate, the nature of the specimen is not indicated.

(a) The dibromide, dissolved in chloroform, was submitted to ozonisation for 24 hours. The crude ozonide obtained on removal of the chloroform was decomposed by gentle warming with water and the decomposition products were extracted with pure ether. The extract was washed with sodium bicarbonate solution, and the ether removed. The residue on distillation yielded the fractions (i) b. p. 50–60°, (ii) b. p. 60–95°, and (iii) b. p. 95–115° at 22 mm. Of these, the first consisted almost wholly of bromoacetone (Found : Br, 56.2. Calc. for  $C_3H_5OBr$  : Br, 58.4%. Semicarbazone, m. p. 143°; mixed m. p. with authentic specimen, 143°) and the last consisted partly of unchanged dibromide. As  $\alpha$ -bromopropionaldehyde, the fission product complementary to bromoacetone, is destroyed by distillation, it was necessary to isolate it as the corresponding acid. Accordingly in another experiment the aqueous liquor containing the decomposed ozonide was allowed to stand with hydrogen peroxide. The product, after the neutral material had been removed in ether, was acidified and thoroughly extracted. The dried extract yielded an acidic liquid, from which fractions of b. p. 90–105°/757 mm. (40–100°/22 mm.) and 100–120°/22 mm. were obtained; the former satisfied no test for formic acid or acetic acid, and the latter, consisting of somewhat impure bromopropionic acid, was readily converted successively into sodium lactate and pyruvic acid (phenylhydrazone, m. p. 191°; mixed m. p. with an authentic specimen, 191°). It was thus established that both fission products of an  $\alpha\delta$ -dibromide were produced in considerable amounts; it remained to search for fission products of an  $\alpha\beta$ - and of a  $\gamma\delta$ -dibromide. Since little success attended the manipulation or attempted isolation of the non-volatile brominated aldehydes and the acids derived therefrom by gentle oxidation, effort was especially directed to the recognition of even traces of formaldehyde (from an  $\alpha\beta$ -dibromide) or of acetaldehyde (from a  $\gamma\delta$ -dibromide). The vapours generated during the hydrolysis of ozonide specimens were therefore swept by a stream of carbon dioxide into water and into an alcoholic solution of  $\beta$ -naphthol. In the many experiments carried out, the formation of neither formaldehyde nor acetaldehyde

could be detected by odour, by the formation of a  $\beta$ -naphthol derivative, or by other tests.

(b) The oxidation of the dibromide by neutral permanganate at  $0^\circ$  (1 atom of oxygen per molecule of dibromide) was carried out in acetone solution in the usual way. After removal of the manganese mud and acetone, the aqueous oxidation liquid deposited a solid and an oily liquid. The former was a solid dibromoglycol, which crystallised from petroleum in colourless prisms, m. p.  $94-95^\circ$  (Found: Br, 58.0.  $C_6H_{12}O_2Br_2$  requires Br, 58.0%); the latter contained bromoacetone (semicarbazone, m. p.  $143^\circ$ ) and unchanged dibromide, both of which were readily separated, but the remaining brominated material decomposed on attempted distillation at 1 mm. pressure. The solid dibromoglycol was  $\beta$ -dibromo- $\delta$ -methylpentane- $\gamma$ -diol. When gently oxidised with aqueous chromic acid, it yielded an oil, the neutral portion of which was bromoacetone and the acidic portion was converted into pyruvic acid by hydrolysis and subsequent oxidation with permanganate. Since the solid dibromoglycol was obtained in much smaller yield than the corresponding compound from  $\alpha$ -dimethylbutadiene, attempts were made to isolate a second isomeric compound. The oxidation products, however, proved too intractable for success in this direction, and attempts to demonstrate by permanganate oxidation anything beyond the fact that a considerable proportion of the dibromide suffered decomposition into the appropriate products proved unprofitable.

*$\beta$ -Dimethylbutadiene.*—The hydrocarbon was prepared from pinacol by the method of Kyriakides (*J. Amer. Chem. Soc.*, 1914, **36**, 987). It was very thoroughly washed, dried, and fractionated; after a final distillation over sodium, it boiled at  $69.5-70^\circ/765$  mm. Yield, 60%.

*Bromination.* The addition of bromine was carried out in chloroform, carbon disulphide, purified petroleum, ether, and hexane, at  $-15^\circ$ . Removal of the solvent under reduced pressure yielded a pale yellow semi-solid mass, from which liquid and solid components were separated by mixing it with light petroleum and freezing out the solid: this was so excessively soluble in the liquid bromide that after six freezings and filtrations only an indifferently good separation was effected. Working without a solvent, or with other solvents, gave even less satisfactory results. The total yield of solid separated was slightly more than 80% of the bromination product. All operations with the bromides were carried out in front of a powerful suction fan on account of their lachrymatory nature.

*The solid portion of the bromination product.* This consisted entirely of the  $\alpha$ -dibromo- $\beta$ -dimethyl- $\Delta^2$ -butene (colourless needles, m. p.  $47^\circ$ . Found: Br, 66.5. Calc.: Br, 66.4%) described

by Kondakov (*loc. cit.*). Concerning its easy and very extensive degradation to bromoacetone by permanganate oxidation and by ozonolysis, our results agreed entirely with those of Kondakov and of Macallum and Whitby (*loc. cit.*).

When heated at  $100^{\circ}$  for 1 hour, the solid dibromide suffered partial conversion into a liquid. This liquid, freed as thoroughly as possible from unchanged solid, amounted to about 18% of the total—a proportion that could not be increased by prolonging the period of heating (decomposition became serious on long heating). It had invariably the correct bromine content and showed no appreciable difference from the directly obtained liquid dibromide when submitted to most of the operations and reactions employed in the examination of the latter. The change produced by heating took place to some extent during distillation, causing the pure substance to boil over a range ( $103\text{--}105^{\circ}/15\text{ mm.}$ ); the distillate yielded a small proportion of oily dibromide.

*The liquid portion of the bromination product.* When strongly cooled, the liquid product solidified to a hard crystalline mass; this rapidly liquefied when the temperature rose, leaving crystals of the solid form temporarily undissolved. It distilled completely between  $101^{\circ}$  and  $105^{\circ}$  at 15 mm., the fractions collected at  $1^{\circ}$  intervals freezing with different degrees of ease. Attempts were made, by distilling a considerable quantity of the liquid dibromide, to isolate a pure compound, but none of the fractions appeared to be free from the solid dibromide: indeed, distillation gave no better separation than filtration and resulted in considerable loss of liquid material by isomerisation. Such isomerisation was readily effected by heating the liquid compound at  $100^{\circ}$  for a few minutes; after dilution and cooling, the solid compound could be filtered off.

*Ozonolysis of the Liquid Bromination Product.*—The liquid, dissolved in chloroform and cooled in an ice-salt mixture, was ozonised for 8 hours. The ozonide decomposed very slowly when gently heated with water, giving a large quantity of resinous material. The aqueous liquor, in which formaldehyde could be detected, was submitted to steam distillation; the volatile degradation products were extracted with ether and fractionated. The distillate comprised (i) bromoacetone, b. p.  $45\text{--}50^{\circ}/16\text{ mm.}$  (semicarbazone, m. p.  $143^{\circ}$ ; Found: Br, 58.6. Calc.: Br, 58.4%); (ii) a bromine-containing mobile liquid, b. p.  $50\text{--}55^{\circ}/16\text{ mm.}$ , which yielded a crystalline precipitate with semicarbazide, the precipitate being halogen-free and giving a red colour with ferric chloride; (iii) a small amount of a mobile bromine-containing liquid, b. p.  $55\text{--}90^{\circ}/16\text{ mm.}$ ; and (iv) a viscous high-boiling fraction which contained some unchanged dibromide but consisted mainly of polymerised material.

The liquid produced by heating the solid dibromide gave exactly similar products, but in neither case was it possible to isolate pure substances directly or indirectly from the distillate.

*Permanganate Oxidation of the Liquid Bromination Product.*—The bromine, in 15–20 g. portions, was suspended in water (or dissolved in acetone) and oxidised with neutral permanganate at 0° (1 atom of oxygen per molecule). The product, worked up in the usual way and freed from traces of acidic matter, was a liquid which yielded on distillation the fractions: (i) bromoacetone, b. p. 45–50°/15 mm.; (ii) and (iii) mobile bromine-containing liquids (partly at least ketonic) similar to the corresponding fractions of the ozonolysis product; (iv) a mobile liquid, b. p. 93°/16 mm., obtained in considerable yield and evidently derived from a dibromoglycol by loss of hydrogen bromide (Found: C, 35.5; H, 5.8; Br, 40.4.  $C_6H_{11}O_2Br$  requires C, 36.9; H, 5.6; Br, 41.0%); (v) a viscous liquid, b. p. 120°/16 mm., apparently derived from a dibromoglycol by loss of hydrogen bromide (Found: C, 33.2; H, 4.9; Br, 45.4%); (vi) a small quantity of a solid dibromoglycol, b. p. 148°/16 mm., which crystallised from petroleum in colourless prisms, m. p. 93° (Found: Br, 57.5.  $C_6H_{12}O_2Br_2$  requires Br, 57.2%). Since this was further oxidisable to bromoacetone, it was *αδ-dibromo-βγ-dihydroxy-βγ-dimethylbutane*. The liquid obtained by heating the solid dibromide yielded similar oxidation products.

For comparison, the solid dibromide was likewise oxidised with permanganate, only 1 atom of oxygen per molecule being used. There were obtained: (i) bromoacetone; (ii) a small amount of viscous liquid, b. p. about 120°/15 mm., which from its nature and composition appeared to be somewhat impure dibromoglycol; (iii) a large amount of the solid dibromoglycol, m. p. 93°, described above. Thus, whereas the solid dibromide yielded two dibromoglycols and some bromoacetone, the liquid yielded (in addition to a minor proportion of the same products) a very considerable proportion of other products, including dihydroxylated compounds which had lost hydrogen bromide. The difference between the oxidation products of the two dibromides was maintained from experiment to experiment; but since permanganate oxidation appeared quite unlikely to furnish conclusive evidence of the constitution of the liquid dibromide, experiments were discontinued.

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LXXIV.—*Properties of Conjugated Compounds. Part IX. The Formation of Bimolecular Reduction Products of Butadiene Acids.*

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EVANS and FARMER (J., 1928, 1644) have shown that the addition of hydrogen to conjugated carbon compounds is not invariably terminal, thus taking the first step towards bringing hydrogen into line with other common addenda. It has now been found that the presence of alkyl groups at different positions in the butadiene chain of  $\beta$ -vinylacrylic acid seems to affect the relative extents to which  $\alpha\beta$ - and  $\alpha\delta$ -dihydrogen derivatives are produced: the crudeness of the method of estimating the proportion of the  $\alpha\beta$ -acid\* (Evans and Farmer, *loc. cit.*), however, prevents any confident application of the results to quantitative discrimination between alkylation effects. It has also been found in experiments with different types of butadiene compound, hydrogenated by the action of different metals, media, etc., that the formation of hydrogenated bimolecular compounds is so common that it must be considered a normal feature of reduction. Since the bimolecular compounds are frequently formed side by side with the simple dihydrogen derivatives, their theoretical significance cannot be neglected in a consideration of the mechanism of hydrogen addition.

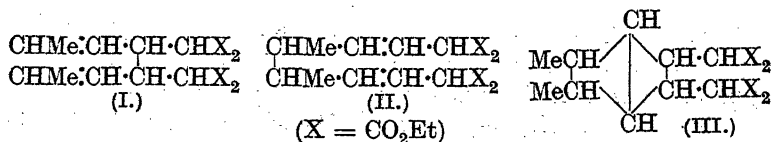
It has been shown that linkage of monohydrogenated molecules may occur at the  $\beta$ -carbon atom of the butadiene chain. Corresponding linkage of reactant molecules might be expected also to be possible at the  $\delta$ - or the  $\zeta$ -carbon atom and the principle entailed would merely represent an extension of that underlying the formation of pinacols and the bimolecular reduction products of mesityl oxide, ethyl  $\alpha$ -cyano- $\beta\beta$ -dimethylacrylate, etc.

Crotylideneacetone and ethyl crotylidenemalonate were the first instances discovered in which there was a definite departure from the rule respecting terminal hydrogen addition. The reduction products from the former of these have already been described, but the constitutions attributed at the same time to those from the

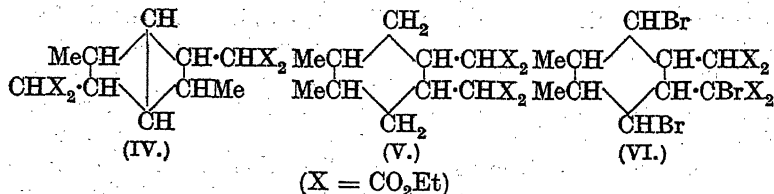
\* The method presents two unsatisfactory features: (1) The acid mixture must be fractionated so thoroughly that no unreduced acid is left behind. It is well-nigh impossible to do this without sacrificing a portion of the distillate and so running the risk of changing the proportion of the isomerides. (2) In addition to the expected acids the permanganate oxidation product yields syrupy residues which survive re-oxidation processes. These are persistently obtained from the alkylsorbic acids.

latter proved so difficult of establishment that an account of the reduction is only now possible.

The unimolecular hydrogenation products from ethyl crotylidene-malonate appear in quite insignificant quantity when aluminium amalgam is the reducing agent; almost the entire product consists of a mixture of two isomeric bimolecular *esters*, one of which is a solid. It was expected that each of these substances would be correctly represented by one or other of the formulæ (I) and (II).



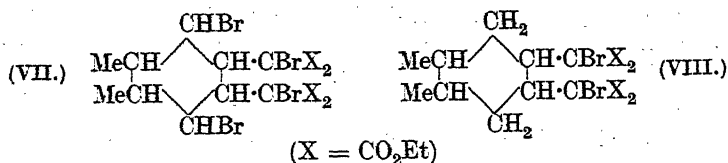
Although the composition of the substances corresponded with this expectation, it soon became obvious that both representations were incorrect. In the first place, both substances were so saturated that they were quite unaffected by permanganate at 20° or by ozone; in the second place, both substances took up two, and *only two*, atoms of hydrogen in the presence of palladium, the hydrogenation being effected with difficulty. The first of these properties could conceivably be the result of steric hindrance, but the two in combination suggested at once the dicyclic constitution (III) for the original compounds (alternatively, but improbably, IV, for one or both) and the monocyclic constitution (V) for their fully reduced derivatives. It was remarkable that with one exception all the



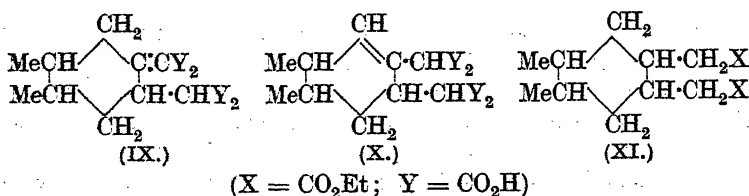
numerous derivatives prepared from the bimolecular compounds were liquids.

In the detailed examination chief attention was paid to the solid compound. This substance absorbed 4 atoms of bromine per molecule to yield a *tribromide* and 6 atoms of bromine (the limit of absorption) to yield a *tetrabromide*. The bromination process was obviously one of combined substitution and addition so that the results corresponded with the formation of (VI) and (VII) from (III). The corresponding fully reduced ester absorbed, in accordance with formula (V), only 4 atoms of bromine per molecule to yield a *di-bromide* representable by (VIII). Attempts were made to oxidise

to carboxyl the bromomalonic groups in the compounds to which formulæ (VII) and (VIII) apply, but oxidation always proceeded irregularly and failed to yield homogeneous products.



The solid bimolecular ester, when hydrolysed with alkali, yielded a mixture of unsaturated tetrabasic acids—liquid and solid: these appeared from their behaviour with permanganate to be representable by (IX) and (X) respectively. The sodium salts of this acid



mixture, when reduced catalytically, yielded a somewhat impure tetrabasic acid, and this, by decarboxylation, a crude dibasic acid the ethyl ester of which agreed in composition with formula (XI). An apparently identical dibasic acid was obtained by hydrolysing and decarboxylating the fully reduced ester (V). If the bimolecular esters were representable by formula (I) or (II), the corresponding saturated dibasic acid would be dipropyladipic or dimethylsuberic acid—acids almost certainly of highly crystalline character.

Although the general behaviour of the solid bimolecular ester corresponded with the constitution (III), it was desired to gain direct evidence of the existence of an intermolecular bridge-bond at the  $\delta$ -carbon atoms of the original butadiene chains. Since regulated oxidation was out of the question, various drastic oxidising agents were tried. With only one of these, hot chromic acid, was there success. This reagent broke down the solid ester to volatile acids and carbon dioxide to the extent of about 96%, but yielded a small quantity of *s*-dimethylsuccinic acid. This acid always appeared if the conditions of oxidation were not greatly changed, but the yield could not be increased.

Most of the experiments carried out with the solid bimolecular ester were also repeated with the isomeric liquid ester. No essential difference in structure between the two compounds (such, for instance, as that holding between III and IV) is adjudged to exist. Probably the two substances are geometrical isomerides, but con-



ditions for oxidising the liquid isomeride to dimethylsuccinic acid were not discovered: under moderately drastic conditions of operation, complete degradation to volatile products ensued.

In the formation of a "para"-bridged cyclohexane derivative from ethyl crotylidenemalonate, the important features from the point of view of additive mechanism are doubtless the attachment of hydrogen at the  $\alpha$ -carbon atoms and the union of the radicals so formed at the  $\beta$ -carbon atoms. The subsequent establishment of bonds between  $\gamma$ - and  $\delta$ -carbon atoms respectively may be regarded as involving an intramolecular variation of the truxillic acid condensation. Therefore, so far as these examples are concerned, true attachment of hydrogenated radicals at the  $\delta$ -carbon atoms remains to be sought.

Ethyl crotylidenecyanoacetate (two forms) has also been reduced: the product consisted mainly of a bimolecular substance very similar in general properties to that from ethyl crotylidenemalonate. Owing to its high boiling point, however, adequate fractionation could not be carried out and detailed examination was abandoned.

The simple butadiene acids which have been reduced— $\beta$ -vinylacrylic, sorbic,  $\alpha$ -methylsorbic, and  $\beta\gamma$ -dimethylsorbic acids—all give considerable yields of high-boiling products which are undoubtedly bimolecular compounds; cinnamylideneacetic acid also gives an intractable acid mixture very different from the dihydrogenated product obtainable with sodium amalgam. It is hoped later to report in detail on some of these substances.

It might be supposed that constitutive influences in the conjugated compound would determine or seriously affect the formation of bimolecular reduction products as well as that of simple  $\alpha\beta$ - and  $\alpha\delta$ -dihydrogen derivatives. Actually, however, the character of the metal and medium employed in reduction appears to exercise a more important influence. Evans and Farmer looked for a difference in the proportion of  $\alpha\beta$ - and  $\alpha\delta$ -dihydrogen derivatives of sorbic and  $\beta$ -vinylacrylic acids to be obtained by using different metals, and media of different acidity (alkalinity), but since the experimental figure for the  $\alpha\beta$ -acid in each case could only be regarded as a lower limit of production, no definite conclusion was possible. Shortly afterwards, however, the appearance of Willstätter, Seitz, and Bumm's paper on the reduction of terephthalic,  $\Delta^{1:3}$ -dihydroterephthalic and  $\Delta^2$ -tetrahydroterephthalic acids (*Ber.*, 1928, **61**, 871) made plain that the character of the reduction product from the first of these is determined by the hydrogen-ion concentration of the medium and that with pure sodium amalgam, under carefully controlled conditions of alkalinity, the last of these may be reduced *more readily* than the corresponding  $\Delta^1$ -acid. Burton and

Ingold (J., 1928, 904) have now recorded figures representing the comparative extents to which the  $\alpha\beta$ -dihydrogen derivatives of sorbic and vinylacrylic acids are formed by sodium in a weakly alkaline and in a weakly acidic medium, but the effect of different metals remains undetermined. From such comparative experiments as have been made by the authors, aluminium amalgam in an aqueous medium appears specially prone to yield bimolecular compounds and all the compounds referred to above can be obtained through its agency. Since a similar state of affairs holds in the reduction of ethylenic acids and ketones by metals, the attribution of reductive polymerisation to a primarily constitutive cause would appear to be ruled out, and consequently the  $\alpha\beta$ ,  $\beta\gamma$ -ratio of simple dihydrogenated molecules (primarily dependent on constitution so far as experiments have yet shown) would seem in all probability to be unaffected by the concurrent formation of bimolecular compounds.

The hydrogenation mechanism suggested by Ingold in discussing the results of Evans and Farmer (*Chem. and Ind.*, 1928, 47, 268) would allow for this probability, but the theoretical basis of the hydrogenation hypothesis subsequently developed (Burton and Ingold, J., 1928, 904; 1929, 2022) appears insufficiently broad to cover Willstätter, Seitz, and Bumm's result with  $\Delta^2$ -tetrahydro-terephthalic acid. (It should be stated, however, that attempts by one of the authors to reduce in similar fashion  $\Delta^8$ -dihydromuconic acid have so far been unsuccessful.)

#### EXPERIMENTAL.

*Reduction of Ethyl Crotylidenemalonate.*—A moist ethereal solution of the ester (prepared by the method of Meerwein, *Annalen*, 1908, 358, 82) was allowed to react with amalgamated aluminium foil for 36 hours. The reduction product was an oil which partly solidified when strongly cooled. The solid portion crystallised from petroleum in stout prisms, m. p.  $61.5^\circ$  (Found: C, 61.8; H, 8.1.  $C_{22}H_{34}O_8$  requires C, 62.0; H, 8.0%), and the liquid distilled as a colourless oil, b. p.  $235\text{--}240^\circ/14$  mm. (Found: C, 61.5; H, 7.8%). These two substances, considered to be isomeric forms of ethyl 1:2-dimethylbicyclohexane-4:5-dimalonate (ethyl butane-2:<sup>3</sup>II:2-cyclobutane-3:4-dimalonate) (III), represented the whole of the reduction product save a very small proportion of low-boiling material. The yield of the solid product was always about 15%.

*Investigation of the Low-boiling Reduction Product.*—This material, accumulated from a series of reductions, was not homogeneous. After several distillations a few grams of liquid, b. p.  $133\text{--}140^\circ/18$  mm., were separated, the first fraction being rejected. Specimens of this substance were oxidised with neutral permanganate in order

to find if simple  $\alpha\beta$ - and  $\alpha\delta$ -dihydrogen derivatives of ethyl crotylidenemalonate were present. Some of the material appeared to be saturated, since considerably less than the calculated quantity of permanganate was reduced. The product, which contained no recognisable trace of succinic acid, consisted of a volatile acid and a little oxalic acid. The former, treated with *p*-bromophenacyl bromide, yielded a solid derivative, which was fractionally crystallised. The *p*-bromophenacyl derivative of acetic acid, m. p. 82—83°, was thus isolated, but the corresponding derivative of propionic acid, which appeared also to be present, could not be separated in pure form. Ozonisation experiments yielded no further information.

*Unsaturation of the Main Reduction Products.*—Both the solid and the liquid substance which constituted the main reduction product remained inappreciably attacked when vigorously shaken with aqueous permanganate at room temperature or when kept in acetone solution in contact with permanganate for several days. Both substances appeared to be little changed by prolonged treatment with ozone, and, even when boiled with permanganate in acetone solution, suffered change extremely slowly. Regulated oxidation was therefore impossible.

Nevertheless, both esters became further hydrogenated when dissolved in alcohol and shaken with hydrogen in the presence of colloidal palladium. Absorption of hydrogen was at first moderately rapid, but the rate decreased until it was barely 1 c.c. per hour. The hydrogen pressure was increased to 2 atmospheres, but still the rate of absorption was very slow. When absorption finally ceased, both esters had taken up the equivalent of two atoms of hydrogen per molecule. Both products, when isolated in the usual way, were colourless oils: that from the solid ester distilled at 225—230°/7 mm. and corresponded in composition with *ethyl 1:2-dimethylcyclohexane-4:5-dimalonate* (V) (Found: C, 61.8; H, 8.6.  $C_{22}H_{36}O_8$  requires C, 61.7; H, 8.5%); that from the liquid ester distilled at 217—223°/13 mm. and was isomeric with the first (Found: C, 61.8; H, 8.2%).

*The Dicyclic Reduction Products.*—(1) *Hydrolysis.* The solid compound (1 mol.) was warmed with alcoholic caustic soda derived from the calculated quantity of sodium (4 atoms). The sodium salt immediately deposited was collected and dissolved in a little water, and the solution evaporated to dryness. The residue, acidified with the calculated quantity of hydrochloric acid and diluted with an equal volume of water, yielded crystals of an acid. These were filtered off and the mother-liquor was thoroughly extracted with ether. The ethereal extract yielded a syrupy acid. Some decarboxylation accompanied hydrolysis.

The solid acid (35% yield), when reprecipitated from ethereal solution by addition of petroleum, formed a crystalline powder, m. p.  $175^{\circ}$  with evolution of carbon dioxide. It was an unsaturated tetrabasic acid, which at  $0^{\circ}$  rapidly decolorised an amount of permanganate equivalent to 3 atoms of oxygen per molecule (more could be reduced slowly). The oxidation product was an enolic syrupy acid of doubtful homogeneity which could not be purified or successfully broken down to known compounds. The solid acid is probably to be represented as 1:2-dimethyl- $\Delta^5$ -cyclohexene-4:5-dimalonic acid (X) (Found: C, 53.5; H, 6.0.  $C_{14}H_{18}O_8$  requires C, 53.5; H, 5.7%).

The liquid acid did not consist entirely of a tetrabasic substance. It readily lost carbon dioxide on heating, rapidly reduced cold permanganate (3 atoms of oxygen per molecule), and yielded an oxidation product somewhat similar to that derived from the solid acid, except that a proportion of oxalic acid was also formed. It probably represented a mixture of partly decarboxylated dimethylcyclohexene- and dimethylcyclohexylidene-dimalonic acids.

The liquid ester also yielded a bulky sodium salt when warmed with alcoholic caustic soda. The acid derived therefrom was wholly syrupy and could not be purified. On oxidation with permanganate the latter yielded some oxalic acid and a large proportion of syrupy acid. Numerous attempts were made to obtain solid or homogeneous liquid acids (a) by the decarboxylation of the tetrabasic acids described above and (b) by the decarboxylation of their oxidation products. All the products, however, were liquid acids of doubtful homogeneity.

(2) *Bromination*. The solid ester (chloroform solution), when treated with the equivalent of 4 atoms of bromine per molecule, yielded an oily tribromo-derivative (Found: Br, 36.6.  $C_{22}H_{33}O_8Br_3$  requires Br, 36.1%), which solidified after long standing; when treated with the equivalent of 6 atoms of bromine, an oily tetrabromide was obtained which would absorb no more bromine (Found: Br, 42.6.  $C_{22}H_{32}O_8Br_4$  requires Br, 43.0%). It was attempted to oxidise the bromomalononic groups of the tetrabromide to carboxyl by gradually adding finely powdered permanganate to an acetone solution of the bromide containing some free caustic alkali. Oxidation proceeded, but the product consisted of some oxalic acid and a large amount of a viscous acid which would not crystallise.

(3) *Degradation*. Since oxidising agents were almost without action on them, the dicyclic esters were subjected to vigorous oxidation with chromic acid. To the solid ester (10 g.), dissolved in glacial acetic acid (160 c.c.), a solution of chromic acid (50 g.) in 50% acetic acid (80 c.c.) was slowly added in small portions, the

mixture being continuously shaken and finally heated on a steam-bath for 1 hour. The product, from which acetic acid was removed by steam distillation, was saturated with sulphur dioxide and kept over-night; the excess of sulphur dioxide was then boiled off and the solution was made alkaline with concentrated aqueous ammonia and filtered. The filtrate, combined with several aqueous extracts of the chromium oxide, was evaporated to small bulk, acidified, and finally evaporated to dryness. The residue, when extracted with ether, gave a small yield of a slightly syrupy, solid acid. This, when drained and recrystallised from ether, formed colourless prisms, m. p.  $192-193^{\circ}$ , which were identified as *trans*-dimethylsuccinic acid (Found: C, 49.5; H, 6.9. Calc.: C, 49.3; H, 6.8%. Mixed m. p. with an authentic specimen,  $192-193^{\circ}$ ).

Similar experiments were carried out with the liquid dicyclic ester, but the conditions for getting even a small yield of a solid degradation product were not found.

*The Monocyclic Products of Complete Reduction.*—(1) *Hydrolysis and decarboxylation.* In attempting to derive 1:2-dimethylcyclohexane-4:5-diacetic acid from the solid dicyclic ester, two methods were employed: (a) the catalytically reduced ester was hydrolysed with the theoretical quantity of alcoholic caustic soda, the derived acid being decarboxylated by heating at  $180^{\circ}$ , and (b) the dicyclic ester was hydrolysed with alcoholic caustic soda, the sodium salt catalytically reduced, and the derived acid decarboxylated by heating to  $180^{\circ}$ . (Re-submission of the decarboxylated acid to hydrogenation resulted in no further absorption of hydrogen.) The crude reduced tetrabasic and dibasic acids obtained in both processes were liquids which showed no tendency to crystallise. No difference was observed between corresponding products and since the second process was the more economical, a considerable quantity of the dibasic acid was thereby prepared. This was esterified with alcohol and hydrogen chloride, and the product distilled. The distillate was a colourless oil, b. p.  $179^{\circ}/9$  mm., which is considered to be *ethyl 1:2-dimethylcyclohexane-4:5-diacetate* (Found: C, 67.45; H, 10.1.  $C_{16}H_{28}O_4$  requires C, 67.55; H, 9.9%). A portion of this ester was re-hydrolysed with alcoholic caustic soda. The free acid was a colourless oil which still showed no tendency to crystallise. Since it could not be distilled, it contained traces of impurity (Found: *M*, dibasic, 237.  $C_{12}H_{20}O_4$  requires *M*, 228).

(2) *Bromination and oxidation.* The fully reduced derivative of the solid dicyclic ester, dissolved in carbon disulphide, absorbed 4 atoms of bromine per molecule (with evolution of hydrogen bromide). The product, *ethyl 1:2-dimethylcyclohexane-4:5-di-*

*bromodimalonate* (VIII), when well washed and freed from solvent, was obtained as a yellow oil (Found: Br, 26.3.  $C_{22}H_{34}O_8Br_2$  requires Br, 27.3%). This was used without further purification in an attempt to oxidise the bromomalononic groups (bromine first being replaced by hydroxyl through the action of cold caustic potash) to carboxyl. Permanganate, dissolved in acetone, was the reagent employed, but oxidation did not proceed smoothly to yield the desired dimethylcyclohexanedicarboxylic acid. As expected, oxalic acid was formed, but the accompanying gummy acid when esterified yielded an ester which was far from homogeneous.

*Ethyl Crotylidenecyanoacetate*.—Crotonaldehyde and ethyl cyanoacetate, mixed in molecular proportion, were cooled to  $-15^\circ$  and a little piperidine was added. The mixture was allowed to attain room temperature and was then kept at  $30^\circ$  for 24 hours. There were two products: (1) a solid which crystallised from petroleum in colourless prisms, m. p.  $57-58^\circ$  (Found: C, 65.6; H, 6.7.  $C_9H_{11}O_2N$  requires C, 65.4; H, 6.7%), and (2) an isomeric liquid, b. p.  $122^\circ/9$  mm. (Found: C, 65.8; H, 6.5%).

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## LXXV.—*The Electrical Conductivities of Solutions of Tetraethylammonium Iodide in Benzonitrile.*

By AUSTIN RAYMOND MARTIN.

WALDEN has shown that the mobility of the tetraethylammonium ion is inversely proportional to the viscosity of the solvent. On the basis of this relationship and a knowledge of the equivalent conductivity at infinite dilution ( $\Lambda_0$ ) of tetraethylammonium iodide in benzonitrile, certain ionic mobilities in this solvent may be determined from the conductivity measurements previously recorded (Martin, J., 1928, 3270). Walden's early measurements of the conductivities of solutions of tetraethylammonium iodide in benzonitrile (*Z. physikal. Chem.*, 1906, 54, 189; 55, 710; see also "Elektrochemie nichtwässeriger Lösungen," 1924, p. 135) are too erratic to give an unequivocal value of  $\Lambda_0$ . Hence the present investigation was undertaken. The degree of dissociation of tetraethylammonium iodide in benzonitrile is also of interest.

## EXPERIMENTAL.

The apparatus and method used were the same as those described previously (Martin, *loc. cit.*).

*Tetraethylammonium Iodide.*—Kahlbaum's product was recrystallised three times from redistilled absolute alcohol, powdered in an agate mortar, and dried by being heated electrically in a vacuum at 100° over phosphoric oxide, the drying agent remaining at room temperature (Found: I, 49.30. Calc.: I, 49.36%). The molecular weight of tetraethylammonium iodide has been taken as 257.13.

*Solvent Correction.*—In series *a* the specific conductivity of the pure solvent at 25° was  $0.99 \times 10^{-7}$  mho, and in series *b*  $0.38 \times 10^{-7}$  mho. The conductivity of the solvent was in all cases subtracted from the observed conductivity in order to obtain the conductivity due to the dissolved salt. In series *a* the largest correction was 1.8% and in series *b* 0.5%.

## Results.

The results of the conductivity measurements are given in Table I. The dilution, in litres, is denoted by *v*, and  $\Delta$  is the difference between the observed value of the equivalent conductivity ( $\Lambda$ ) and the straight line obtained by plotting  $\Lambda$  against the square root of the concentration ( $\sqrt{c}$ ), a positive sign before  $\Delta$  indicating that the observed point is above the straight line.

TABLE I.

Temp. 0°.				Temp. 25°.			
Series.	<i>v</i> .	$\Lambda$ .	$\Delta$ .	Series.	<i>v</i> .	$\Lambda$ .	$\Delta$ .
<i>b</i>	98.95	21.74	—	<i>b</i>	101.10	34.00	—
<i>a</i>	100.20	21.85	—	<i>a</i>	102.38	34.08	—
<i>c</i>	115.50	22.47	—	<i>c</i>	118.02	35.01	—
<i>a</i>	506.9	27.87	−0.10	<i>a</i>	517.9	43.53	±0.00
<i>b</i>	758.5	28.83	±0.00	<i>b</i>	775.0	45.27	±0.00
<i>a</i>	2030	30.82	+0.09	<i>a</i>	2074	48.32	+0.01
<i>b</i>	3754	31.42	−0.07	<i>b</i>	3836	49.53	−0.04
<i>b</i>	7579	32.15	±0.00	<i>b</i>	7744	50.62	±0.00
<i>a</i>	9558	32.32	+0.03	<i>a</i>	9766	50.94	+0.05
Temp. 50°.				Temp. 70°.			
<i>b</i>	103.45	47.15	—	<i>b</i>	105.36	58.15	—
<i>a</i>	104.75	47.29	—	<i>a</i>	106.69	58.37	—
<i>a</i>	529.9	60.99	±0.00	<i>a</i>	539.7	75.83	±0.00
<i>b</i>	793.0	63.60	±0.00	<i>b</i>	807.6	79.06	−0.09
<i>a</i>	2122	68.33	+0.12	<i>a</i>	2,161	85.38	+0.42?
<i>b</i>	3925	70.01	−0.12	<i>b</i>	3,997	87.38	±0.00
<i>b</i>	7924	71.70	±0.00	<i>b</i>	8,070	89.39	±0.00
<i>a</i>	9992	71.98	−0.14	<i>a</i>	10,178	90.04	+0.14

The values of  $\Lambda$  at even dilutions are given in Table II. Interpolation was carried out on a  $\Lambda$ -log *c* graph.

TABLE II.

$\Lambda$ .					$\Lambda$ .				
$v$ .	0°.	25°.	50°.	70°.	$v$ .	0°.	25°.	50°.	70°.
100	21.79	33.93	46.88	57.50	2,000	30.73	48.22	67.97	84.73
200	24.73	38.29	52.95	65.57	5,000	31.78	50.00	70.68	88.08
500	27.67	43.34	60.55	75.15	10,000	32.36	50.92	72.14	89.88
1000	29.47	46.22	64.88	80.65					

*Extrapolation to  $\Lambda_0$ .* The square-root law was used to extrapolate to  $\Lambda_0$ . Ferguson and Vogel's method (*Phil. Mag.*, 1925, 1, 971) gave values of the index  $n$  in the formula,  $\Lambda_0 = \Lambda + ac^n$ , which were so close to 0.5 (namely, 0.507, 0.502, 0.491, 0.500) that this equation led to practically the same values of  $\Lambda_0$  as the square-root law. The values of  $\Lambda_0$  are:

Temp. ....	0°	25°	50°	70°
$\Lambda_0$ .....	33.71	53.13	75.47	94.12

#### Discussion.

*Values of  $\Lambda_0$ .*—The values of the product of  $\Lambda_0$  and the viscosity of the solvent ( $\eta$ ) at the same temperature are given below. The constancy of this product shows the exactness to which  $\Lambda_0$  is proportional to the fluidity of the solvent as the temperature is varied. The values of the viscosity of benzonitrile used were those determined previously (Martin, *loc. cit.*).

Temp. ....	0°	25°	50°	70°
$\Lambda_0\eta$ .....	0.65	0.66	0.66	0.63

In Table III are the ratios of the values of  $\Lambda_0$  of tetraethylammonium iodide in benzonitrile to the values at the same temperatures in acetone, acetonitrile, and ethylene chloride, the only solvents for which modern data are available. The ratios of the fluidities of the solvents are also given. The data for acetone are those of Walden, Ulich, and Busch (*Z. physikal. Chem.*, 1926, 123, 429), for acetonitrile those of Walden and Birr (*ibid.*, 1929, A, 144, 269), and for ethylene chloride those of Walden and Busch (*ibid.*, 140, 89). Extrapolation to  $\Lambda_0$  was in all cases carried out by the square-root law.

TABLE III.

Temp.	$\frac{\Lambda_0 \text{ PhCN}}{\Lambda_0 \text{ Me}_2\text{CO}}$	$\frac{\eta \text{ Me}_2\text{CO}}{\eta \text{ PhCN}}$	$\frac{\Lambda_0 \text{ PhCN}}{\Lambda_0 \text{ MeCN}}$	$\frac{\eta \text{ MeCN}}{\eta \text{ PhCN}}$	$\frac{\Lambda_0 \text{ PhCN}}{\Lambda_0 \text{ C}_2\text{H}_4\text{Cl}_2}$	$\frac{\eta \text{ C}_2\text{H}_4\text{Cl}_2}{\eta \text{ PhCN}}$
0°	0.203	0.204				
25	0.254	0.255	0.284	0.277	0.695	0.633
50	0.295	0.292				

*Ionic Mobilities in Benzonitrile.*—On the assumption that the mobility of the tetraethylammonium ion is given by the relation (Walden and Birr, *Z. physikal. Chem.*, 1929, A, 144, 308),

$$\text{Mobility} \times \text{Viscosity of solvent} = 0.296,$$



its mobility in benzonitrile has been calculated, and from Kohlrausch's law of the independent migration of ions and the data recorded previously, the ionic mobilities given in Table IV were obtained. In calculating the mobilities of the silver and nitrate ions, Koch's value, 0.475 (determined from *E.M.F.* measurements; J., 1928, 524), was used for the transport number of the silver ion in silver nitrate. In the rows designated *l* are the ionic mobilities, and in those designated *r'* are the apparent values of the ionic radii calculated from these mobilities on the assumptions (i) that the only resistance to the motion of the ions at infinite dilution is the viscous drag of the solvent, and (ii) that the magnitude of this drag is given by Stokes's law. In the rows *r* are the ionic radii obtained from crystal data by Goldschmidt (*Trans. Faraday Soc.*, 1929, 25, 253); both *r* and *r'* are expressed in Ångström units.

TABLE IV.

Temperature.					Temperature.						
Ion.	0°.	25°.	50°.	70°.	Ion.	0°.	25°.	50°.	70°.		
NEt <sub>4</sub>	<i>l</i>	15.26	23.87	33.79	44.45	Ag <sup>+</sup>	<i>l</i>	15.82	24.78	—	—
	<i>r'</i>	2.75	2.75	2.75	2.75		<i>r'</i>	2.65	2.65	—	—
K <sup>+</sup>	<i>l</i>	13.70	21.85	—	40.31	I <sup>-</sup>	<i>r</i>	1.13	—	—	—
	<i>r'</i>	3.06	3.01	—	3.03		<i>l</i>	18.45	29.26	41.68	49.67
Na <sup>+</sup>	<i>r</i>	1.33	—	—	—	<i>r'</i>	2.28	2.24	2.23	2.46	
	<i>l</i>	12.06	18.31	25.11	32.67	<i>r</i>	2.20	—	—	—	
	<i>r'</i>	3.48	3.59	3.70	3.74	Br <sup>-</sup>	<i>l</i>	12.36	19.44	27.39	—
	<i>r</i>	0.98	—	—	—		<i>r'</i>	3.40	3.38	3.39	—
Li <sup>+</sup>	<i>l</i>	10.84	16.73	22.70	—	NO <sub>3</sub> <sup>-</sup>	<i>r</i>	1.96	—	—	—
	<i>r'</i>	3.87	3.93	4.10	—		<i>l</i>	17.48	27.40	—	—
	<i>r</i>	0.78	—	—	—	<i>r'</i>	2.40	2.40	—	—	

The differences between *r* and *r'* cannot be used to calculate the degree of chemical solvation of the ions, since Born has shown (*Z. Physik*, 1920, 1, 220) that on physical grounds a difference is to be expected, owing to the fact that the dipolar solvent molecules take a finite time to orient themselves in the ionic field as the ion moves through the solvent. However, the physical theory is not sufficiently developed to be used for the quantitative interpretation of the present results.

*Dissociation of Tetraethylammonium Iodide in Benzonitrile.*—The observed slopes of the  $\Lambda - \sqrt{c}$  straight lines are given below, together with those calculated from the Debye-Hückel-Onsager equation

$$\Lambda = \Lambda_0 - \left[ \frac{5.78 \times 10^5}{(DT)^{3/2}} \Lambda_0 + \frac{58.0}{(DT)^{1/2} \eta} \right] \sqrt{2c}$$

where *D* = the dielectric constant of the solvent,  $\eta$  = the viscosity of the solvent, and *T* = the absolute temperature.

The author is indebted to Dr. A. O. Ball for the values of  $D$ .

Temp. ....	0°	25°	50°	70°
$D$ .....	27.58	25.22	23.31	21.98
Slope, obs. ....	133.6	217.6	332.1	423.3
Slope, calc. ....	90.9	147.3	202.4	259.4

The values of the degrees of dissociation,  $\alpha$ , and of the corresponding dissociation constants,  $K$  (corrected for activity), calculated by the method given previously (Martin, *loc. cit.*), are set out in Table V. The Debye-Hückel equations used for calculating the ionic activity coefficients ( $\gamma$ ) were (after insertion of numerical values):  $-\log_{10} \gamma = 2.78\sqrt{c'} - 9.66c'$  at 0°;  $= 2.78\sqrt{c'} - 9.69c'$  at 25°;  $= 2.78\sqrt{c'} - 9.66c'$  at 50°;  $= 2.77\sqrt{c'} - 9.63c'$  at 70°;  $c'$  being the ionic concentration.

TABLE V.

Dilution (litres).

Temp.		2000.	1000.	500.	200.	100.	Mean.
0°	$\alpha$	0.9688	0.9516	0.9288	0.8947	0.8619	—
	$K \cdot 10^3$	12	13	15	20	24	17
25	$\alpha$	0.9667	0.9524	0.9249	0.8833	0.8594	—
	$K \cdot 10^3$	11	14	14	17	23	16
50	$\alpha$	0.9568	0.9366	0.9056	0.8502	0.8210	—
	$K \cdot 10^3$	8	10	11	12	17	12
70	$\alpha$	0.9580	0.9385	0.9044	0.8493	0.8132	—
	$K \cdot 10^3$	9	10	11	12	16	12

It is not unlikely that at a dilution of 100 litres the Debye-Hückel-Onsager equation gives too large a value for the diminution in conductivity resulting from the interionic Coulomb forces, perhaps owing to the neglect of higher terms. For  $K$  increases at this dilution; and completely dissociated salts such as potassium and sodium chlorides in aqueous and methyl-alcoholic solutions at dilutions less than 100 and 300 litres, respectively, have values of  $\Lambda$  greater than those calculated from this equation (Onsager, *Trans. Faraday Soc.*, 1927, 23, 341). These deviations from the predicted values are, however, much smaller than those in the opposite direction in the cases of thallium chloride and silver nitrate resulting from incomplete dissociation.

If the foregoing mean values of the dissociation constants be compared with those of the iodides of lithium, sodium, and potassium, lithium bromide, and silver nitrate (Martin, *Phil. Mag.*, 1929, 8, 547), it is seen that in benzonitrile tetraethylammonium iodide is a stronger electrolyte than any of these salts, although it is apparently only slightly stronger than sodium iodide.

Calculation by means of the van 't Hoff isochore from the variation

of the dissociation constant with temperature indicates that the heat change in the dissociation of tetraethylammonium iodide in benzonitrile is an evolution of approximately 1 kg.-cal. per mol.

*Summary.*

1. The electrical conductivities of solutions of tetraethylammonium iodide in benzonitrile have been measured at 0°, 25°, 50°, and 70° over the range of dilution 100 to 10,000 litres.

2. By utilising the fact that the mobility of the tetraethylammonium ion is inversely proportional to the viscosity of the solvent, together with data previously recorded, certain ionic mobilities in benzonitrile have been determined.

3. The electrolytic dissociation of tetraethylammonium iodide in benzonitrile has been investigated.

The author wishes to thank Professor J. C. Philip, F.R.S., for very kindly placing at his disposal facilities for carrying out this work.

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LXXVI.—*Investigations on the Bivalency of Carbon.*  
*Part III. Some Experiments on Xanthhydrol,*  
*Dixanthhydril Ether, and Xanthhydril Chloride.*

By FREDERIC GORONWY KNY-JONES and  
ALLAN MILES WARD.

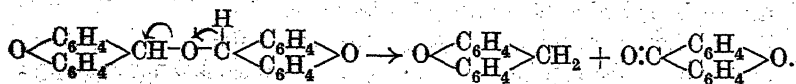
XANTHHYDROL and benzhydrol being very similar in their properties, an attempt was made to study quantitatively the rate of displacement of chlorine from xanthhydril chloride as in the case of diphenylchloromethane (Ward, J., 1927, 2285). In lime-dried ethyl alcohol at room temperature, however, the chloride lost its halogen immediately and completely as hydrogen chloride, the reactivity appearing to be exactly comparable with that of triphenylmethyl chloride.

Xanthhydril chloride reacted readily with water at room temperature, giving xanthone and xanthen in approximately equal quantities, together with some xanthhydrol. As was to be expected in view of this result, xanthhydrol was readily decomposed by hydrochloric acid, being changed completely to equal quantities of xanthone and xanthen after 5 minutes' boiling with *N*/100-acid: it was, however, not attacked by boiling *N*/10-sodium hydroxide. Dibenzhydril ether (Ward, *loc. cit.*) was formed from benzhydrol

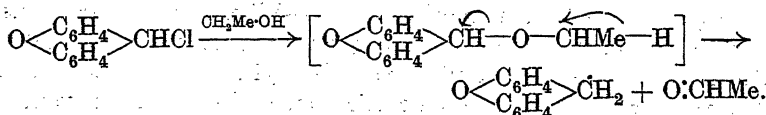
by boiling with dilute acids, but it was stable to boiling *N*/100-acid : such acid converted dioxanthhydryl ether into xanthone and xanthen (equal quantities) in  $\frac{1}{2}$  hour.

The reactions with alcohol are analogous. Xanthhydryl chloride and ethyl alcohol yielded xanthen as the main product, and some xanthone. (The alcoholic solution restored the colour to Schiff's reagent, but responded to no other test for acetaldehyde : compare Fosse, *Compt. rend.*, 1901, **133**, 880; *Bull. Soc. chim.*, 1906, **35**, 1005.) Xanthhydrol also was completely converted into xanthen (main product) and xanthone on being boiled with *N*/20-ethyl-alcoholic hydrogen chloride for 1 hour. The change was incomplete after shorter times of heating. Xanthhydrol, therefore, is much more stable in the presence of alcoholic than of aqueous hydrogen chloride. Dioxanthhydryl ether, which is insoluble in ethyl alcohol, dissolved readily on being boiled with ethyl-alcoholic hydrogen chloride (*N*/20) for a few minutes : the solution remained homogeneous when cooled to room temperature and the product was xanthhydrol (yield, at least 89% of the theoretical).

Xanthhydrol, dioxanthhydryl ether, and xanthhydryl chloride, therefore, are far more reactive than benzhydrol, dibenzhydryl ether, and diphenylchloromethane. Although, however, diphenylmethane and benzophenone are not produced from the last three compounds under the conditions under which xanthen and xanthone are produced from the first three, they can be obtained by reactions at higher temperatures (see, *e.g.*, Nef, *Annalen*, 1897, **298**, 234; also in the thio-series, Schönberg, Schütz, Bruckner, and Peter, *Ber.*, 1929, **62**, 2550). In connexion with the preceding transformations in ethyl alcohol, the observations of Bacon (*Amer. Chem. J.*, 1905, **33**, 92), Goldthwaite (*ibid.*, 1903, **30**, 461), and Norris and Young (*J. Amer. Chem. Soc.*, 1924, **46**, 2580) on the pyrogenic decomposition of arylalkyl alkyl ethers are of interest. Kauffmann and Pannwitz (*Ber.*, 1912, **45**, 766) have shown that triarylcarbinols in general are reduced to the corresponding triarylmethanes by alcoholic hydrogen chloride or by formic acid, and triphenylmethyl chloride in pure ethereal solution in the presence of zinc chloride (Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 204) or aluminium chloride (Norris and Young, *loc. cit.*) decomposes into triphenylmethane and acetaldehyde, doubtless by a similar mechanism (see also Hardy, *J.*, 1929, 1000). The scheme which has been used to explain these decompositions would in the case of dioxanthhydryl ether be as follows :



The instability of dixanthhydryl ether in the presence of acids finds a parallel in the decomposition of bistriphenylmethyl ether (Gomberg, *loc. cit.*); the acids he used were, however, more concentrated and the product was triphenylcarbinol. The reaction between xanthhydryl chloride and ethyl alcohol may be assumed to proceed *via* the ethyl ether, which, however, has not been isolated :



It appears highly probable, therefore, that the displacement mechanisms for systems  $\text{CHR}_1\text{R}_2\text{X}$  and  $\text{CR}_1\text{R}_2\text{R}_3\text{X}$  are closely allied. The displacements of halogen which have been studied for some systems  $\text{CHR}_1\text{R}_2\text{Cl}$  may be interpreted as proceeding through a phase  $\text{R}_1\text{R}_2\text{C}^<$ , but an hypothesis involving the ion  $\text{CR}_1\text{R}_2\text{H}^+$  will also provide an explanation (Ward, *loc. cit.*, p. 2287). The bivalent-carbon hypothesis is impossible for systems of the triphenylmethane type, and a larger range of reactions can be interpreted on the ionisation theory. Certain reactions which have been regarded as evidence of the formation of ions in the triphenylmethane series were observed in the xanthhydryl experiments. Conant and Evans (*J. Amer. Chem. Soc.*, 1929, **51**, 1934), for example, consider that the presence of free radicals is indicated by the precipitation of Prussian blue when a chloroform solution of the material under investigation is shaken with an aqueous solution of potassium ferricyanide and ferric chloride. Dixanthhydryl ether readily brings about this reaction. Further, Boyd and Hardy (*J.*, 1928, 632) attribute to ionisation the red colour developed when triphenylcarbinol is dissolved in a mixture of sulphuric and acetic acids:  $\text{Ph}_3\text{C}\cdot\text{O}\cdot\text{SO}_3\text{H} \rightleftharpoons \text{Ph}_3\text{C}^+ + \text{SO}_4\text{H}^-$ . The colour may be due to a quinonoid tautomeride of this ion (see Gomberg and Sullivan, *J. Amer. Chem. Soc.*, 1922, **44**, 1810; Gomberg and Blicke, *ibid.*, 1923, **45**, 1765). The development and subsequent disappearance of a yellow-green colour in all the experiments in hydrochloric acid here described may therefore be evidence of the presence of the ion  $\text{O} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CH}^+$ . Conant and Sloan (*ibid.*, 1923, **45**, 2468) consider that they have obtained the free xanthyl radical in an impure state.

The accumulated evidence supports the ionisation theory rather than the theory of bivalent carbon. As applied to the problem of the Walden inversion (Ward, *J.*, 1927, 445), the latter theory is now recognised to be untenable (see also the criticism of Ashworth and Burkhardt, *J.*, 1928, 1795): three groups, and not two, must be

momentarily attached to the asymmetric carbon atom during the transformations, and evidence has been obtained that optical activity can persist under such conditions (McKenzie, Roger, and Wills, J., 1926, 779).

#### EXPERIMENTAL.

*Preparation of Dixanthhydrl Ether.*—When xanthhydrol was heated with petroleum for several days (Meyer and Saul, *Ber.*, 1893, 26, 1276), the conversion into dixanthhydrl ether was incomplete. The preparation was therefore carried out by heating moist xanthhydrol, prepared from xanthone (25 g.), at 150–155°, and finally at 175° for 1½ hours. The product was cooled, powdered, and extracted three times with methylated spirit. The residue (19.1 g.), m. p. 193–209°, was crystallised from 200 c.c. of xylene, washed with the same substance and with ether, and air-dried (yield, 17.8 g.); m. p. 205–211°. A sample of the dixanthhydrl ether, twice recrystallised from xylene, well washed with ether, and dried in a desiccator over paraffin wax, melted at 219° (Meyer and Saul, *loc. cit.*, give m. p. about 200°) (Found: C, 82.4; H, 5.0. Calc.: C, 82.5; H, 4.8%).

*Preparation of Xanthhydrl Chloride.*—(1) Thionyl chloride (2 c.c.), dissolved in 50 c.c. of light petroleum (b. p. 40–60°), reacted readily with dixanthhydrl ether (5 g.) suspended in the solution; as, however, needle-shaped crystals soon began to separate, the mixture was gently refluxed for 15 minutes until only a small amount of brown solid remained in suspension. The colourless solution was cooled in ether-solid carbon dioxide, and the crystals thus produced were collected and recrystallised repeatedly from 100 c.c. of the same solvent, long colourless needles being obtained. The solvent was removed as completely as possible in an atmosphere of nitrogen and the crystals were dried in a stream of the warmed gas (yield, 3–3.5 g.). The crystals became discoloured on drying and decomposition doubtless took place, but they could be kept unchanged for days in contact with light petroleum (Found, by titration of the hydrogen chloride liberated in alcoholic solution: Cl, 14.8, 15.0, 16.1, 13.8. Calc.: Cl, 16.4%).

The product melted at 60–65° after softening at 50°: selected crystals melted above 70°, e.g., 71–73°, 72–74.5° (Gomberg and Cone, *Annalen*, 1910, 376, 188, give m. p. 73–75° after sintering at 71°). Colourless crystals when removed from the mother-liquor became yellow on drying in the air and then colourless again; they were unmelted at 100° and kept their needle shape.

(2) The same results were obtained by the interaction of xanthhydrol and thionyl chloride in boiling light petroleum.

*Reaction between Xanthhydrol and Hydrochloric Acid.*—(a) Xanthhydrol, prepared from xanthone (5 g.), was washed with water and refluxed for 1 hour with 75 c.c. of *N*/100-hydrochloric acid. The solid melted and needle-shaped crystals then separated. They were removed from the cooled solution, washed with water, and immediately heated to boiling with 30 c.c. of methylated spirit. The solution was cooled to room temperature, filtered from the crop of crystals, added to an equal bulk of glacial acetic acid containing 5 c.c. of a concentrated aqueous solution of urea, and poured after 2 hours into excess of water. The precipitate then formed was collected, washed with water, and added to the crop of crystals above. The whole was dried over calcium chloride (yield, 5.15 g.) and extracted four times with 40–50 c.c. of boiling light petroleum (b. p. 40–60°). The extracts were well cooled and filtered, and the combined filtrates evaporated to dryness, leaving 2.42 g. of colourless solid, m. p. 94–96°, mixed m. p. with xanthen (m. p. 100–101°) 96–97.5°. Two further similar extractions of the undissolved solid gave 0.09 g., m. p. 97–135°, and a seventh extraction gave 0.05 g., m. p. 142–158°. The remaining undissolved solid (2.46 g.) melted alone at 163–168°, and at 167–170° when mixed with xanthone (m. p. 174°).

This method of separating xanthen from xanthone, although not quantitative, since xanthone was slightly soluble in the light petroleum used, was the one that gave the best results. The steam-distillation method used by Heller and Kostanecki (*Ber.*, 1908, 41, 1325) is unsatisfactory because xanthone is slightly volatile in steam.

(b) Xanthhydrol (0.5 g.) was boiled with *N*/100-hydrochloric acid (7.5 c.c.) for 5 minutes; the subsequent procedure was as described under (a). The alcoholic filtrate, after being added to the urea-glacial acetic acid, was still clear after 7 hours, whereas a portion of the same preparation of xanthhydrol, when dissolved in methylated spirit and added to the urea-acetic acid solution, was converted into a stiff paste after a few minutes.

(c) Similar experiments were carried out with hydrochloric acid, the strength being gradually increased to 5*N*; xanthen and xanthone were the only products isolated.

*Xanthhydrol and Aqueous Sodium Hydroxide.*—Xanthhydrol (0.5 g.) was boiled with 7.5 c.c. of *N*/10-aqueous sodium hydroxide for 1 hour. No yellow-green colour appeared and the xanthhydrol did not melt as in the hydrochloric acid reactions. The solid dissolved completely in about 10 c.c. of cold methylated spirit and the addition of this solution to the urea reagent gave a precipitate comparable in amount with that obtained on testing the xanthhydrol in (b).

*Reaction between Dixanthhydryl Ether and Hydrochloric Acid.*—(d) Dixanthhydryl ether (5 g.) was boiled with *N*/2-hydrochloric acid (75 c.c.) for 1 hour. The products were examined and separated as in (a); xanthhydrol was not present. The product (2.16 g.) obtained from the first four extractions melted at 97–98°, and at 98–99° when mixed with xanthen; the seventh extract (0.02 g.) had m. p. 163–166°. The remaining portion (2.35 g.), insoluble in the light petroleum, melted at 165–169°, and at 169–172° when mixed with xanthone.

(e) Finely powdered dixanthhydryl ether (0.5 g.) was boiled with *N*/100-hydrochloric acid (7.5 c.c.) for 15 minutes. The solution was cooled, and the product, which contained needle-shaped crystals, was collected, washed with water, and boiled with alcohol (15 c.c.). A part, doubtless unchanged ether, did not dissolve. The alcoholic solution did not give the urea reaction for xanthhydrol, but yielded a copious white precipitate on being poured into water.

(f) This experiment was carried out as in (e), but the mixture was boiled for  $\frac{1}{2}$  hour. The product dissolved completely in 5 c.c. of hot ethyl alcohol; the solution thus formed gave a crop of colourless needles on cooling, and the filtrate did not contain any xanthhydrol.

*Reaction between Xanthhydryl Chloride and Water.*—Xanthhydryl chloride (2 g.; Cl, 14.8%) was triturated with 30 c.c. of water at room temperature for  $\frac{1}{2}$  hour. The chloride, initially yellow-brown, rapidly became almost colourless. The products, collected and washed with water, were extracted with 30–40 c.c. of methylated spirit and the alcoholic solution was added to the urea reagent: a precipitate separated. Two more extractions of the residue were made and the precipitates were collected after some hours, washed with methylated spirit, and dried (total yield, 0.43 g., corresponding to 0.41 g. of xanthhydrol). The solutions and the remaining residue were worked up as in (a), the following yields being obtained: (i) 0.56 g., m. p. 94–96°, (ii) 0.05 g., m. p. 165–167°, (iii) 0.53 g., m. p. 168–170°.

*Reaction between Xanthhydrol and Ethyl-alcoholic Hydrogen Chloride.*—(g) Xanthhydrol (0.2 g.), dried over stick sodium hydroxide, was dissolved in ethyl-alcoholic hydrogen chloride (*N*/10 approx., prepared by passing hydrogen chloride into lime-dried ethyl alcohol) and boiled for 5 minutes. The cooled solution was tested for xanthhydrol and gave a copious precipitate. When the reaction mixture was boiled for 15 or for 30 minutes, there was also a positive test, but the amount of condensation product which separated in the latter case was small. Heating for 1 hour brought about complete decomposition of the xanthhydrol.



(h) Xanthhydrol (2.5 g.) was boiled with 20 c.c. of *N*/20-ethyl-alcoholic hydrogen chloride for 1 hour. The solvent was then distilled: it restored the colour to Schiff's reagent, but only slightly reduced ammoniacal silver nitrate. The solid residue was dried over calcium chloride (yield, 2.4 g.) and examined in the usual way. It gave: (i) 1.36 g., m. p. 93—95°, mixed m. p. with xanthen, 94—96°; (ii) 0.09 g., m. p. 142—164°; (iii) 0.80 g., m. p. 163—166°, mixed m. p. with xanthone, 168—171°.

*Reaction between Dixanthhydryl Ether and Ethyl-alcoholic Hydrogen Chloride.*—Dixanthhydryl ether (2 g.), when boiled with *N*/20-ethyl-alcoholic hydrogen chloride (20 c.c.), dissolved after 4 minutes, and solid did not separate when the solution was cooled. An equal volume of the urea reagent was added; a copious white precipitate, which separated after a few minutes, was collected after 14 hours and washed repeatedly with methylated spirit until the washings gave only a small precipitate on being poured into water. The product, after being dried over calcium chloride, weighed 1.98 g. (equivalent to 1.87 g. of xanthhydrol).

The alcoholic-acetic acid solution and washings did not give any precipitate on being further tested for xanthhydrol and were therefore poured into excess of water. The precipitate was collected and dissolved in about 30 c.c. of hot methylated spirit. Fine colourless needles (0.12 g.), which separated from the cooled solution, did not melt at 225°, and gave a copious evolution of ammonia on fusion with potash (this product is possibly formed from urea and xanthhydrol by the condensation of one molecule of each). When excess of water was added to the methylated spirit solution, a solid (0.26 g.) was obtained which began to melt at 90° but was not completely molten at 220°; it probably consisted mainly of xanthen and xanthone.

*Reaction between Xanthhydryl Chloride and Ethyl Alcohol.*—Lime-dried ethyl alcohol (about 50 c.c.) was added to a light petroleum solution of xanthhydryl chloride (prepared from 5 g. of xanthhydrol). The solution, which became successively brown and green, was shaken for a few minutes, and the solvent then distilled off. The green residue was dried in a current of air (yield, 4.1 g.). A portion of it (about 0.2 g.), tested for xanthhydrol, did not give a precipitate after 4 hours. The remainder was extracted four times with light petroleum. The soluble portion (3.05 g.) was yellow-brown and melted at 85—90°; it was dissolved in light petroleum and refluxed (charcoal) for  $\frac{1}{2}$  hour. The pale yellow solution thus formed was filtered and evaporated; yield, 2.65 g., m. p. 91—93°; mixed m. p. with xanthen 97—99°. The green insoluble portion (0.58 g.) melted at 143—146°; it dissolved in acetone to a green solution, from which

the colour was removed by means of charcoal. The purified product had m. p. 171—172° and mixed m. p. with xanthone 173—174°.

One of us (A. M. W.) is indebted to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of the materials.

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# LXXVII.—*The Apparent Hydration of Ions. Part IV. The Densities and Viscosities of Saturated Solutions of Silver Nitrate in Nitric Acid.*

By JOHN WILLIAM INGHAM.

THE investigations in this series already described have dealt with solutions of alkali-metal and ammonium chlorides in hydrochloric acid (Parts I and II, J., 1928, 1917, 2381; Part III, J., 1929, 2059). The present paper deals with an extension of the work to solutions in nitric acid, the solute being silver nitrate, a choice which allows of accurate analytical control and is also convenient for comparison with the salt and acid pairs previously examined. The silver ion, having a radius of 1.13 Å.U. (Goldschmidt, *Trans. Faraday Soc.*, 1929, 25, 253), which is between those of the sodium and potassium ions ( $\text{Na}^+$  0.98,  $\text{K}^+$  1.33), might be expected to show hydration effects of an intermediate nature. The nitrate ion, which resembles the chlorine ion in probably being not hydrated but differs from it in having a more complex and less symmetrical structure, might show specific effects due to these features. Differences might also be expected for these two ions on the basis of Sugden's theory (J., 1926, 174) that anions have not all the same activity as depolymerisers of the solvent.

The experimental work consisted of the determination of the densities and viscosities at 25° for a series of solutions of acid content covering the range 0—12*N*, and saturated with silver nitrate. A parallel series of determinations with acid alone was also made. The same apparatus was used as in the previous work, but a slight modification was made by placing the gauge for the Scarpa viscometer in the thermostat and substituting water for alcohol in it, thus making the control more certain. The results are in Tables I and II, concentrations being in mols./litre. The viscosities of the pure nitric acid solutions were determined both by the Scarpa and by the Ostwald U-tube method.

TABLE I.

$d_4^{25}$ .	$10^5\eta$ .	HNO <sub>3</sub> .	AgNO <sub>3</sub> .	Total solute.	H <sub>2</sub> O.	Total solution.	Col. 8.
2.2969	2989	—	9.714	9.714	35.9	45.6	55.33
1.7376	1852	2.222	4.952	7.174	42.0	49.1	54.1
1.6343	1712	2.797	4.047	6.844	42.8	49.6	53.7
1.4669	1523	4.282	2.456	6.738	43.3	50.0	52.5
1.4236	1508	5.010	1.975	6.985	42.9	49.9	51.8
1.4014	1512	5.599	1.685	7.284	42.3	49.6	51.3
1.3742	1578	6.976	1.185	8.161	40.7	48.9	50.1
1.3690	1630	7.971	0.943	8.914	39.2	48.1	49.1
1.3695	1712	9.093	0.724	9.82	37.4	47.2	48.0
1.3741	1784	10.12	0.589	10.71	35.3	46.0	46.6
1.3856	1883	11.69	0.393	12.08	32.3	44.4	44.8

TABLE II.

$d_4^{25}$ .	$10^5\eta$ .		HNO <sub>3</sub> .	H <sub>2</sub> O.	Total solution.
	(Scarpa).	(Ostwald).			
0.99707	891	891	—	55.35	55.35
1.0297	917	914	0.987	53.7	54.7
1.0633	954	951	2.010	52.0	54.0
1.0892	989	991	2.810	50.6	53.4
1.1193	1049	1042	3.744	49.0	52.8
1.1542	1123	1120	4.863	47.1	51.9
1.1787	1195	1187	5.667	45.6	51.3
1.2245	1335	1327	7.257	42.6	49.9
1.2678	1497	1487	8.900	39.2	48.1
1.3397	1764	1758	11.92	32.7	44.6

Col. 8 of Table I gives the sum of Cols. 4, 5, and 6; on the assumption that the solutes are completely dissociated and that the hydrogen ions are present as  $H_3O^+$  ions (or, alternatively, that they have no effective size as free individuals), these figures give the relative numbers of particles having effective volume, the water molecules being treated as unpolymerised and no allowance being made for hydration of the silver ions. Col. 6 in Table II gives the corresponding figures for the pure acid solutions, the values in this case being identical with "Total solution."

### Discussion of Results.

*Densities and Solution Volumes.*—The data in Col. 8, Table I, and Col. 6, Table II, show a close parallelism and, when plotted against acid normalities, give graphs which are superimposable except in the region 0–5*N*, where the solutions containing silver nitrate have slightly higher numbers of "effective particles" (the maximum divergence being 0.3 unit/litre). The saturated solution of silver nitrate in pure water, having 55.33 for this number, may be compared with pure water itself, for which the value is 55.35. If the solution volume of the water were the same in the two cases, then that of the silver nitrate would be exactly twice as much. Caution must, however, be observed in making such deductions,

and due regard must be given to the possibility of an alteration in the values for the water molecule itself. For instance, a change of the condition of the solvent, such as depolymerisation, might lead to an adjustment of the volume effectively shown. Similarly, the packing of ions amongst the water molecules and the interactions of "hydration" will undoubtedly lead to modifications of the volume which the solvent molecule apparently occupies. These various effects may all be regarded as readjustments of the amount of "free space" in the liquids. This free space is normally included in the apparent solution volumes of the constituents of a solution, whether solute or solvent. Usually, in dealing with aqueous solutions, a constant value is assumed for the water, based upon the density of the pure solvent, and any variations are arbitrarily expressed as those of the solute: an example is that of lithium chloride (Green, J., 1908, 93, 2023), discussed by the author in Part II (*loc. cit.*). On the other hand, the type of expression suggested by Masson (J., 1911, 99, 1132), and used in the present series of investigations, makes provision for changes in the apparent solution volume of the solvent in the solution as compared with the pure liquid. The solution volumes deduced by these methods all include a proportion of "free space" except for the two smallest ions  $\text{Li}^+$  and  $\text{Na}^+$ , in which cases the apparent solution volumes were found to be less than the gram-ionic volumes calculable from lattice radii. These are the ions which definitely show hydration effects. The case of the ammonium ion was especially interesting, for it gave an unexpectedly high solution volume of 19.64 c.c. (Part III), compared with the value 7.43 c.c. deduced from the ionic radius. At the same time, this ion was shown to have a negative effect on the viscosity. It is suggested that the appropriation of this large amount of free space, accompanied by a repulsion of the solvent molecules, causes the ammonium ion to show a lower viscous effect than its apparent solution volume would otherwise indicate. The ammonium ion, in fact, behaves as a "loose spot" (compare Part II).

The application of Masson's formula,  $d_r^s = K + k_1a + k_2b$ , to the data of Table I may now be considered. The series of densities resembles that for the  $\text{NaCl-HCl}$  and  $\text{KCl-HCl}$  mixtures (Part I), there being a minimum value; since, however, the data for silver nitrate cover a much wider range of salt concentrations, it is not surprising that the formula has a more restricted application. Constants were determined by (i) the method of least squares and (ii) Campbell's method (see Part III, *loc. cit.*), the corresponding equations being

$$(i) \ d_r^s = 1.0350 + 0.02647a + 0.1299b;$$

$$(ii) \ d_r^s = 1.0306 + 0.02702a + 0.1305b.$$

The second of these is preferred, and the densities calculated by means of it compare well with those observed except for the end values of the series; *e.g.*,

$\bar{d}_4^{25}$ (obs.)	2.2969	1.7376	1.6343	1.4669	1.4236
„ (calc.)	2.2986	1.7368	1.6343	1.4669	1.4236
$\bar{d}_4^{25}$ (obs.)	1.4014	1.3742	1.3690	1.3695	1.3741
„ (calc.)	1.4017	1.3737	1.3690	1.3706	1.3808

The solution volumes corresponding to the constants of the equations differ only slightly according to the equation used, thus:

	AgNO <sub>3</sub> .	HNO <sub>3</sub> .	H <sub>2</sub> O.
(i)	38.66	35.32	17.41
(ii)	38.14	34.92	17.48

The values may be compared with those derived from other sources. Jabczyński, in a paper on the dimensions of ions in aqueous solutions (*Rocz. Chem.*, 1923, **3**, 362), has discussed the data for many salts, including nitrates and chlorides. He gives the solid volume of silver nitrate as 39.04, and calculates the upper and lower limiting solution volumes to be  $w_1$  39.34 and  $w_0$  25.91, respectively, these being deduced from data by means of empirical formulæ, and the solution volumes being calculated from density data by means of the ordinary equation  $w = \frac{1}{N} \left( 1000 - \frac{1000d - MN}{d_0} \right)$ , where  $d_0$  is the density of pure water. The lower limiting values  $w_0$  were, for the chlorides of sodium potassium, caesium, and rubidium, shown to agree with the molecular volumes calculated from the lattice radii of the ions as given by Bragg (*Phil. Mag.*, 1920, **40**, 169), but the revised data for the radii nullify this agreement, which in any case did not extend to other salts. The agreement found between the upper limiting values  $w_1$  and the solid volumes in the case of many salts, including silver nitrate, is apparently significant, although too much importance must not be attached to it, since the result is obtained by neglecting the effect of changes of the packing arrangements upon the volume occupied by the water. All that can be safely concluded is that, in solutions of high concentration, the solution volume of the salt approaches that of the solid in many cases, and if the ionic radii remain the same, the "free space" associated with the ions in solution is of the same order as that for the solid state. The mean value deduced for silver nitrate in the mixed salt and acid solutions, *viz.*, 38.40, is thus seen to be satisfactory. The fact that the value remains constant over the greater part of the series may be attributed to the relatively small variation in total solute strength, so that the apparent volume of the nitrate ion, which accounts for the major portion of the total volume of the salt, remains constant. This

would not be the case in a simple series of solutions of silver nitrate alone, varying over the same range of salt concentration, *viz.*, 0—10*N* (app.), as in the mixtures. The same argument applies to the acid itself, so the acid volume deduced for the mixed solutions will not be expected to apply to any considerable part of Table II. Actually, it does apply for the concentration region 6—9*N*, for which solutions the densities can be fairly accurately calculated by the formula  $d_{25}^{25} = 1.0306 + 0.02702a$ , but outside these limits there is rapid divergence.

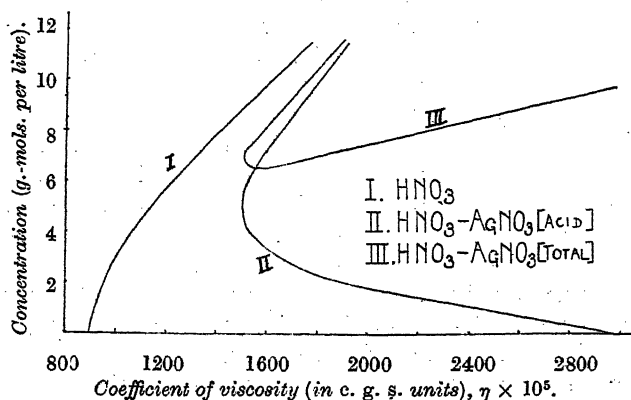
The difference (3.28) between the means of the above values of the volumes, *viz.*,  $\phi'_{\text{AgNO}_3} = 38.40$ ,  $\phi'_{\text{HNO}_3} = 35.12$ , is taken as the volume of the silver ion, and  $\phi'_{\text{HNO}_3}$  will be provisionally assumed to be the value of  $\phi'_{\text{NO}_3}$  also.\* The value for the silver ion falls between those obtained for Na<sup>+</sup> (1.58) and K<sup>+</sup> (12.25) in Part I. Furthermore, if these values are used to derive values for the nitrate ion from the limiting values of sodium and potassium nitrates given by Jabickyński, *viz.*,  $w_1(\text{NaNO}_3) = 37.87$ ,  $w_1(\text{KNO}_3) = 47.61$ , the values for this ion are 36.29 and 35.36, respectively, the latter being in very close agreement with the value deduced above. In this connexion, it may be noted that lithium nitrate ( $w_1$  30.24) is not in agreement. This again is probably due to the method of obtaining the solution volumes without regard to changes of the water volume. In the case of lithium chloride (Part II, *loc. cit.*), it was shown that for a 5.407*N*-solution, the solution volume (22.43) obtained by using a density for water of 1.01275 was considerably higher than either the solid volume (20.94) or the solution volume (20.24 at 5*N*) calculated by Green (*loc. cit.*). A difference in the assumed density of the solvent water of about 1% therefore makes a considerable difference to the calculated salt volumes, and this is most marked for lithium salts, so the above apparent discrepancy of lithium nitrate is probably capable of a similar explanation.

The solution volumes of the silver and nitrate ions, *viz.*, 3.28 and 35.12 respectively, may be compared with ionic volumes deduced from lattice radii. For the former ion, the values given by Goldschmidt (*loc. cit.*), 1.13, and by Pauling, 1.26 (quoted by Goldschmidt), lead to gram-ionic volumes of 3.665 and 5.079 respectively. The value 3.28 now found for the solution volume is thus, as with lithium and sodium ions, less than that calculated from the lattice radius. The nitrate ion has a structure with the centres of the four atoms in one plane, the oxygen atom centres being at the corners of an equilateral triangle, and that of the nitrogen atom being at the mid-point (Bragg, *Phil. Mag.*, 1926, 2, 258). The

\*  $\phi$  is used for the volume of ions added to 1 c.c. of solution;  $\phi'$  is used for the gram-ionic volume of an ion.

inter-atomic distances of the oxygen atoms are given as 2.25 Å.U. and their radii as 1.35 Å.U. These dimensions imply a very close packing of the oxygen atoms round the central nitrogen atom, with considerable deformation of the former. These results have been confirmed and amplified in a comprehensive survey of the type of compound  $ABX_3$  by Zachariassen (*Norske Videnskaps-Akad.*, 1928, 1, *mat.-nat. Klasse*, 4). Thus, in lithium nitrate the distance from an oxygen centre to the nitrogen centre is 1.25 Å.U., which is practically the same as in the Bragg structure. It appears to be well established that both the nitrate ion and the carbonate ion, which has almost identical dimensions, preserve well-defined identities. The exact volume occupied by such an ion is not easy to determine, but as an upper limit that of the triangular prism con-

FIG. 1.



taining it may be taken. This is calculated to be 34.4 for the gram-ion. Actually, this will be somewhat high, and if the lower limit be chosen as the volume of three oxygen atoms ( $r = 1.32$ ), giving 17.5, it seems probable that the true volume will lie between these two limits. The solution volume determined is actually quite close to the upper limit thus obtained, and it will be shown that the volume influence of this ion upon viscosity is of the same order.

*Viscosities.*—The graphs of the data shown in Fig. 1 may be compared with those in Fig. 2, Part II, for hydrochloric acid solutions alone or containing sodium chloride. Aqueous hydrochloric acid solutions have higher viscosities than those of nitric acid of equal normality. Nitric acid appears to have a simpler behaviour, the curve being linear above 5*N*. Starting from pure water and comparing the two acids, it is found that the viscosity differences at corresponding normalities (i) at first increase from 42 ( $\times 10^{-5}$ ) units

at  $N = 1$  to 73 at  $N = 3$ ; (ii) they then diminish until the value 43 is again reached at  $N = 8$ , after which (iii) there is a rapid increase to 146 at  $N = 12$ . These effects might be interpreted as being due to (i) a more rapid depolymerisation of the water by nitrate than by chlorine ions in the earlier stages of  $1-3N$ ; (ii) the influence of the larger size of the former ion tending to a greater viscosity effect and hence a making up of some of the ground lost during the initial period; (iii) the entry of some specific effect in the solutions of high concentration of hydrochloric acid which is not paralleled in those of nitric acid or else is offset by a difference in the numbers of particles of all kinds, which numbers are considerably less in the case of nitric acid. The effective numbers of particles as defined by Col. 6, Table II, for nitric acid, and falling from 55.35 to 44.60, show much greater variation than for hydrochloric acid, for which (from Green's data) the range is 55.35—53.24 for the corresponding range 0—12*N*. Another possible factor causing such differences of behaviour would be incomplete ionisation of the nitric acid in solutions of high concentration, since, as will be shown later, the increase of viscosity caused by adding a given ion is partly dependent upon the strength of the field into which it is placed. There is, however, no evidence that nitric acid is less dissociated than hydrochloric acid and, in fact, the behaviour in dilute solutions suggests the complete dissociation of both acids (MacInnes and Cowperthwaite, *Trans. Faraday Soc.*, 1927, 23, 400).

The most noteworthy feature in the graphs for the silver nitrate-nitric acid solutions is the obvious similarity to those for sodium chloride in hydrochloric acid, both sets showing the approach to a minimum viscosity as salt is replaced by acid. It should be noted that the minimum does not occur at the point of minimum total solute concentration.

The linear relation for nitric acid of concentrations exceeding 5*N* is expressed by

$$\eta = 0.006822 + 0.0009077C$$

for the Scarpa series (if the mean of the Scarpa and Ostwald series is taken, the first constant becomes 0.006787). If this equation is compared with one of the form deduced by Einstein (*Ann. Physik*, 1906, 19, 289), viz.,  $\eta = \eta_0 [1 + \text{constant} \times \phi]$ , and if it be assumed that the nitrate ions contribute the main effect in altering the viscosities in proportion to their volume, so that  $\phi = C\phi'/1000$ ,  $\phi'$  is given by  $[0.0009077 \times 1000]/[0.006787 \times (\text{constant})]$ . If the value 4.5 be taken for the constant in the Einstein equation (compare Hatschek, *Trans. Faraday Soc.*, 1913, 9, 80),  $\phi_{\text{NO}_3}$  becomes 29.7 c.c. and  $\eta_0$  would be 0.006787. It might be argued that the latter quantity represents the fundamental viscosity of depolymerised



water at 25°, and hence it might be used to calculate the degree of polymerisation in ordinary water by comparing it with the viscosity of ordinary water and employing the equation  $\eta = \eta_0 (1 + 2.55\phi)$ , which with the constant 2.55 might be considered applicable to the case of the uncharged water polymerides. This calculation, with  $\eta_w = 0.00891$ , gives  $\phi$  as 0.1225 c.c., or 122.5 c.c. per litre, corresponding with a polymerisation of 12.3%. The significance of the value of  $\eta_0$  as thus suggested is open to question, for at present there is no evidence of its applicability to solutions other than those here considered. Further, the equation  $\eta = \eta_0 (1 + 4.5\phi)$  is not satisfactory either for the data for the mixed solutions of silver nitrate and nitric acid or for correlating hydrochloric acid and the mixed chloride solutions. It may be compared with the equation of Smoluchowski (*Kolloid-Z.*, 1916, 18, 194) put in the form  $\eta = \eta_0 \{1 + 2.5\phi (1 + x)\}$ , where the term  $(1 + x)$  takes account of the effect of the charge on the particles and presumably varies with the total number of these. If it is accepted that the volume 29.7 c.c. represents the effective value for the nitrate ion, then the factor  $(1 + x)$  for nitric acid solutions of 5*N* upwards remains constant and equal to 4.5/2.5. This again assumes the fundamental significance of  $\eta_0$ . It is probable, therefore, that the linear relationship for nitric acid is due to a balance of a number of effects, and is not to be interpreted fully on these simple lines.

Since a satisfactory interpretation of the data for the mixed solutions could not be obtained on the above lines, recourse was had to the empirical equation,  $\eta_2 - \eta_1 = \frac{1}{2}(\eta_2 + \eta_1)2.5\phi$ , employed in previous parts of this series. According to this formula a change of viscosity occasioned by the addition of a quantity of ions of nett volume  $\phi$  is proportional to that volume and to the mean viscosity of the solutions concerned. It appears that introduction of the mean viscosity in this way is equivalent to making allowance for the effect of the charges on the ions, but in a different way from that of Smoluchowski. Thus the effect of an addition  $\phi$  is greater in solutions of high total-ion strength than in those of lower concentration. By applying this to the solutions of nitric acid alone, in the first case, and using successive pairs of values from Table II, the  $\phi'$  values of the nitrate ion are calculated. Thus, from the fourth and fifth experiments (Scarpa values)

$$\eta_1 = 0.00989; \quad \eta_2 = 0.01049; \quad \eta_2 - \eta_1 = 0.00060; \quad \eta_2 + \eta_1 = 0.02038; \quad C_2 - C_1 = 0.934;$$

$$\phi' = \frac{\Delta\eta \times 1000 \times 2}{2.5 \times (\eta_2 + \eta_1)\Delta C} = \frac{0.00060 \times 2000}{2.5 \times 0.02038 \times 0.934} = 25.23.$$

and the values for the complete series are as follows:

$C$ .....	0	0.987	2.010	2.810	3.744	4.863	5.667
$\phi'$ .....	11.7	15.5	18.0	25.2	24.4	30.9	
$C$ .....	5.667	7.257	8.900	11.92			
$\phi'$ .....	27.8	27.9	27.3				

The mean value for  $C > 5N$  is  $\phi' = 27.6$ , which may be compared with that derived directly from the linear relationship discussed above, viz., 29.7: these values fall between the limits already adduced for the volume of this ion and they approximate to the solution volume found. These facts, in conjunction with the fair constancy of the values in the above table for solutions of concentrations above  $3N$ , are taken to indicate an absence of hydration effects for the nitrate ion. The initial rise in the series is attributed to the depolymerising action of this ion, whereby the apparent  $\phi'$  value is reduced. The tendency for the values to fall, over the range  $5-12N$ , may be connected with the falling off in the total number of particles present. An alternative explanation might be that incomplete ionisation in the very concentrated solutions causes an apparent reduction of the effective volume—an actual reduction due to changes in the packing arrangements of the ions and water molecules and equivalent to a loss of free space is not excluded. In this connexion, the difference between nitric and hydrochloric acids is noteworthy. It was shown that with the latter (Part I) the  $\phi'$  value of the chlorine ion (22.43) which could be used to account for the viscosities of solutions of  $3-6N$  on the above lines was quite inadequate for the values at higher concentrations, and the apparent  $\phi'$  values would rapidly increase with increasing acidity, this being due apparently to some specific effect such as the formation of a complex molecule (?  $H_3OCl$ ) which has no parallel in the nitric acid solutions.

The value 28 being accepted for the effective volume of the nitrate ion in solutions containing that ion in concentrations from  $7$  to  $10N$ , the data of Table I may be used to calculate the apparent  $\phi'$  values for the silver ions in the mixed solutions of total concentrations between these limits. Thus, for the first pair of solutions there is a fall in viscosity accompanying a fall in concentration of  $2.540$  in the nitrate ion and of  $4.762$  in the silver ion, and the calculation is made as follows :

$$\begin{aligned}\eta_1 &= 0.02989; \Delta\eta = 0.01137; \\ \eta_2 &= 0.01852; (\eta_1 + \eta_2) = 0.04841;\end{aligned}$$

$$1000 \phi = \frac{0.01137 \times 2000}{0.04841 \times 2.5} = 187.9 \text{ c.c. per litre.}$$

The total  $\phi$  of  $187.9$  c.c. per litre is reduced by that of the nitrate

ions, *viz.*,  $2.540 \times 28 = 71.1$  c.c., and the difference ( $187.9 - 71.1 = 116.8$  c.c.) divided by the fall in the silver-ion concentration (4.762) gives the effective volume of the silver gram-ion, *i.e.*,  $\phi'_{Ag} = 24.53$  c.c. This may be taken to represent the mean effective volume of the hydrated silver ion for the particular range considered, and the apparent hydration may be calculated after subtracting the volume of the silver ion, 3.28, derived from the densities. Each successive pair of solutions in Table I might thus be treated, but in that part of the table embracing the minimum point of viscosity,  $\Delta\eta$  becomes inconveniently small, hence in this region wider steps have been used. Further, for certain pairs, *e.g.*, the sixth and seventh solutions,  $\eta$  increases whilst  $C_{NO_3}$  increases and  $C_{Ag}$  diminishes, so the  $\phi$  value calculated is the nett effect  $\phi_{NO_3} - \phi_{Ag}$ , and the subsequent calculation of  $\phi_{Ag}$  must be modified accordingly. The series of values relating to the different parts of the table may now be considered, the ordinal numbers referring to the successive pairs of solutions. The values in brackets are indirectly derived, being weighted values deduced from others first obtained from wider steps of the table;  $h$  is the hydration factor or apparent hydration.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
$\phi'_{Ag}$ .....	24.5	24.5	27.5	[25]	20	19	22]	26.2	26.6
$h$ .....	1.21	1.21	1.38	1.24	0.95	0.90			

This series of values may be compared with that obtained for sodium ions in sodium chloride-hydrochloric acid solutions (Table VI; Part I), which commences at 32.0 for the pure saturated solution and falls to 23.5 at the point of minimum viscosity. After this point is reached, in both cases the values begin to rise, but, as the concentrations of the salts are then becoming low, the values may be subject to considerable error partly owing to the smallness of the effects actually attributable to these ions, and partly because other specific effects coming into play in solutions of higher acidities are automatically included in the values for the metal ions. Only the first portion of the series of figures for silver nitrate is therefore useful for the discussion of the hydration. The calculated hydration factors are lower than those obtained for sodium ions at corresponding parts of the series. The initial tendency to rise may be due to the very considerable fall in total solute strength of the solutions in the early parts of the series. This effect is very slight or non-existent in the case of sodium ions. The method of treatment given places the silver ion between the ions of sodium and potassium as regards hydration, in agreement with the idea that the order should be that of the ionic radii, the smaller the radius the greater being the tendency for hydration.

*Summary and Conclusions.*

Determinations have been made at 25° of the solubility of silver nitrate in aqueous nitric acid of concentrations up to 12*N*. The densities and the viscosities of the solutions have been measured together with those of a comparable series for the acid alone.

The formula  $d = K + k_1a + k_2b$  applies to the densities of the mixed solutions of total solute concentration below 9*N*, *a* and *b* being the concentrations of acid and salt respectively. The constants *K* and *k*<sub>1</sub> also apply to the pure acid solutions of concentrations 6–9*N*. The corresponding solution volumes are discussed and compared with those derived by other investigators. The silver ion behaves like lithium and sodium ions in having an apparent volume less than that calculated from its radius in the crystal lattice.

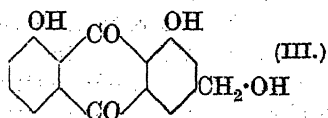
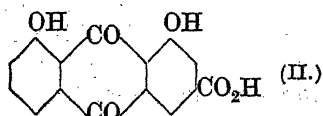
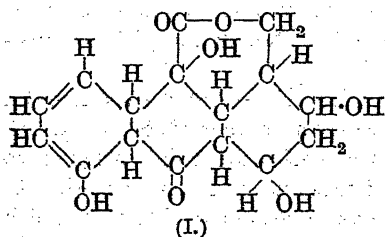
The viscosity data are interpreted by means of the empirical formula  $\eta_2 - \eta_1 = \frac{1}{2}(\eta_2 + \eta_1)2.5\phi$ . A change of viscosity caused by the addition to a solution of ions of volume  $\phi$  is proportional to this volume but also depends upon the mean viscosity of the solutions considered. It is suggested that this latter factor takes account of the electrical effects, and hence the equation allows of the volume effect being separately estimated. The formula, which has previously been applied only to chlorides and their ions, is now found to give a satisfactory account of the data for nitric acid and for its mixed solutions with silver nitrate. The volume effect of the nitrate ion remains substantially constant except in 0–5*N*-solutions of the acid alone, where apparent variations due to the depolymerising action of the ion are indicated. This depolymerisation of the water is more easily effected by the nitrate ion than by the chlorine ion. The volume of the nitrate ion determined from the viscosities approximates to the solution volume calculated from the densities and is also in agreement with values deduced from the data for the size of this ion in crystals; hence it is concluded that this ion is not hydrated. Nitric acid shows a less complex behaviour in solutions of high concentration than does hydrochloric acid, and this suggests the absence of complex ions in the former case.

The silver ions in the mixed solutions show effects attributable to hydration, which is less than that previously found for sodium but greater than for potassium, and this is in accordance with the expected results deduced from the sizes of the ions. Hydration factors for silver ions varying from 1.4–0.90 are found, whereas those for sodium ions were 1.7–1.2.

LXXVIII.—*Experiments on the Constitution of the Aloins. Part II.*

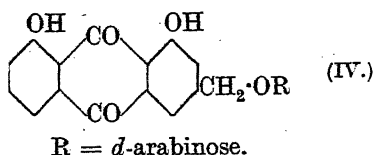
By CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN.

SOME years ago Robinson and Simonsen (J., 1909, 95, 1085) suggested tentatively for barbaloin the formula (I), based chiefly on the following facts: (i) the careful investigations of Jowett and Potter (J., 1905, 87, 878) had shown that barbaloin has the composition  $C_{16}H_{18}O_7$  and contains four hydroxyl groups; (ii) the oxidation of acetylbarbaloin with chromic acid yields a mixture of acetylrhein and acetylaloe-emodin; (iii) rhein was shown to be a dihydroxy-anthraquinonecarboxylic acid, and aloe-emodin the corresponding primary alcohol. At the time, it was considered probable that rhein was an *isochryszazinc*carboxylic acid, but the further work of Robinson and Simonsen, in the publication of the results of which they were anticipated by other workers (Oesterle and co-workers, *Arch. Pharm.*, 1909, 247, 417, 532; 1911, 250, 305), showed that rhein (II) and aloe-emodin (III) are derivatives of chrysazin.



This conclusion obviously necessitated a revision of the suggested constitution for barbaloin and it has only recently been possible to resume the investigation. In the meantime, Léger (*inter alia*, *Ann. Chim.*, 1916, 6, 318; 1917, 8, 265) has published the results of a prolonged investigation of the constitution of barbaloin and of other members of this group. He concludes that the composition of barbaloin is not  $C_{16}H_{18}O_7$  with four hydroxyl groups but  $C_{20}H_{18}O_9$  having five hydroxyl groups. Elementary analysis of either the parent substance or of certain of its simple derivatives does not distinguish between these two formulæ, and Léger was led to make the change by the important observation that when barbaloin is treated with alcoholic hydrochloric acid under specified conditions *d*-arabinose is formed in addition to aloe-emodin. He naturally concluded that barbaloin is the arabinoside of aloe-emodin.

having the constitution (IV), although the actual position of attachment of the sugar residue was not definitely proved.



The suggestion that barbaloin was a glucoside was not new, since Rochleder and Czumpelik (*Monatsh.*, 1863, **44**, 493; 1866, **47**, 119) had observed the formation of a sugar in addition to a yellow crystalline substance by the action of alcoholic hydrochloric acid on barbaloin: Tschirch and Pedersen (*Arch. Pharm.*, 1898, **236**, 206), however, were unable to confirm this. Léger conclusively proved that *d*-arabinose is formed when barbaloin is kept with alcoholic hydrochloric acid for a period of six months, and we have confirmed this. The rate of hydrolysis, if such it be, is extraordinarily slow and very little action appears to have taken place after a week's continuous digestion, although the barbaloin is completely in solution. Léger also observed that aloe-emodin and *d*-arabinose are produced when barbaloin is oxidised with sodium peroxide. In this reaction the sodium peroxide must be assumed to act as a hydrolytic agent, although the yield of aloe-emodin does not exceed 9%.

We have confirmed in all respects Léger's excellent experimental work, but it appears to us that there are a number of cogent reasons for doubting the correctness of the constitution he assigned to barbaloin. The more important of these may be summarised. As already mentioned, elementary analysis does not readily distinguish between the two formulæ which have been suggested, and if the tendency for barbaloin to retain solvent of crystallisation be taken into consideration the differences between the carbon and hydrogen contents lie within the limits of experimental error ( $C_{16}H_{18}O_7$  requires C, 59.6; H, 5.6%.  $C_{20}H_{18}O_9$  requires C, 59.7; H, 4.6%). Molecular-weight determinations have led to contradictory results. By the cryoscopic method, using phenol as the solvent, Jowett and Potter obtained the value 310. On the other hand, Seel and Kelber (*Ber.*, 1916, **49**, 2364) obtained the abnormal value of 197 with phenol; by the ebullioscopic method, however, they obtained the average values of 408 with acetone and 440 with ethyl alcohol. Although the last-mentioned results support the  $C_{20}$  formula, the analytical data for the chloro- and bromo-barbaloins, which are highly crystalline and readily purified substances, agree much more closely with the  $C_{16}$  formula; this is seen from the following

analytical results from the papers of Jowett and Potter and of Léger :

Chlorobarbaloin.				
	% C.	% H.	% Cl.	% Br.
Found .....	45.9	3.4	24.9, 25.1	
Calc. for $C_{16}H_{15}O_7Cl_3$ .....	45.3	3.1	25.1	
Calc. for $C_{20}H_{14}O_8Cl_4$ .....	44.4	2.6	26.3	
Bromobarbaloin.				
Found .....	34.1	2.7		42.9, 41.8, 43.1
Calc. for $C_{16}H_{15}O_7Br_3$ .....	34.3	2.7		42.9
Calc. for $C_{20}H_{14}O_8Br_4$ .....	33.4	1.9		44.6

Jowett and Potter determined the molecular weight of the bromo-compound in phenol by the cryoscopic method and obtained the value 535 ( $C_{16}H_{15}O_7Br_3$  requires  $M$ , 559).

We have obtained analytical results for the bromo-compound (Found : Br, 42.6%) in agreement with those of previous investigators : the compound can be recrystallised without change from pyridine and digested for a short time with diethylaniline; further, its acetyl derivative both before and after treatment with sodium acetate in alcoholic solution has the same composition agreeing with the  $C_{16}$  formula. We are unable, therefore, to accept Léger's suggestion that the marked deficiency in halogen content for the  $C_{20}$  formula may be explained by the instability of the bromo- and chloro-compounds and their tendency to lose hydrogen halides.

Even more remarkable, in our opinion, is the resistance which barbaloin as a simple arabinoside shows to hydrolytic agents, a property which is shared by bromobarbaloin. The latter can be heated in a sealed tube at  $100^\circ$  with alcoholic sulphuric acid (20% by weight) without change. Again, barbaloin and its halogen derivatives dissolve in alkali, yielding bright yellow solutions: these would not be expected if the parent substance were a dihydroxyanthraquinone glucoside with two free phenolic hydroxyl groups, since such substances give red solutions.

We were therefore led to take up again the study of the chemistry of barbaloin and the results so far obtained appear to indicate that Léger's formula cannot be correct.

The action of reducing agents on barbaloin was first investigated, but with unsatisfactory results. The alcohol cannot be reduced with hydrogen in the presence of platinum oxide,\* and on treatment with sodium and alcohol or with hydriodic acid and phosphorus it yields bright red products resembling the phlobaphenes in properties. Acetylation-reduction yielded a colourless gum which could not be purified.

Results of a greater interest have been obtained from a detailed study of the bromination of barbaloin. It has long been known

\* We are indebted to Dr. H. King for carrying out this experiment.

that barbaloin on bromination with bromine water yields a bromo-barbaloin which is either tribromo- or tetrabromo-barbaloin according as the  $C_{16}$  or the  $C_{20}$  formula be adopted. Léger prepared a second bromo-compound, by bromination in hydrobromic acid solution, which differed completely in its properties from the ordinary bromobarbaloin and was considered by him to be the tribromide having the formula  $C_{20}H_{15}O_9Br_3$ . We have prepared this bromo-compound and confirmed its composition, but, on acetylation, contrary to expectation, it yields an amorphous *hexa-acetyl* and not a penta-acetyl derivative. The presence of six hydroxyl groups in this bromo-compound has been confirmed by the preparation of a *pentamethyl* ether by methylation with methyl sulphate, and as this ether can be acetylated it still contains a hydroxyl group. The analytical data (see p. 559) appear to indicate also that a methyl group is introduced into the nucleus, and the pentamethyl ether may therefore be formulated  $C_{20}H_8O_3Br_3Me(OH)(OMe)_5$ . The introduction of a methyl group into the nucleus does not require comment at this stage, since it is not infrequently observed when methyl sulphate is employed as a methylating agent.

These results rendered necessary the careful investigation of ordinary bromobarbaloin, which according to Léger is a tetrabromo-derivative. The difference in physical properties of the two bromo-compounds is very marked: the tribromo-compound is very sparingly soluble and microcrystalline, whereas the tetrabromo-compound is readily soluble and highly crystalline. This differentiation is much greater than that usually observed between tri- and tetra-bromo-derivatives. Our confirmation of the analytical results of previous workers for ordinary bromobarbaloin has been supplemented by molecular-weight determinations kindly carried out by Dr. Sugden by a new ebullioscopic method which he will describe. With acetone as the solvent, the molecular weight was found to be 538, in fair agreement with the calculated value 559 ( $C_{16}$  formula). When the bromo-compound is acetylated with acetyl chloride, a tetra-acetyl derivative, which has been previously described, is obtained, but if acetic anhydride is employed a different *acetyl* derivative is formed. Although this is amorphous, the analytical data show conclusively that it must contain five acetyl groups. The presence of five hydroxyl groups in this bromo-compound was confirmed by the preparation of a *pentamethyl* ether. This, like the acetyl derivative, is amorphous, but the analytical results indicate clearly that its composition is  $C_{16}H_{10}O_2Br_3(OMe)_5$ .

The result of the investigation of the bromo-compounds leads to the apparently anomalous position that, whereas by bromination in aqueous solution derivatives of a substance having the composition



$C_{16}H_{18}O_7$ , are obtained, bromination in the presence of hydrobromic acid yields derivatives of a substance having the composition  $C_{20}H_{18}O_9$ . It seems to us that these results can be reconciled only by assuming that the bromo-compound prepared in hydrobromic acid is a true derivative of barbaloin. As suggested by Léger, barbaloin has, therefore, the composition  $C_{20}H_{18}O_9$ , but it contains not five but six hydroxyl groups, so the formula may be written as  $C_{20}H_{12}O_3(OH)_6$  and that of the tribromo-compound as  $C_{20}H_9O_3Br_3(OH)_6$ .

With regard to the bromo-compound prepared in aqueous solution we suggest that it is an *oxidation product* formed by the loss of four carbon and two oxygen atoms and that it has the composition  $C_{16}H_{10}O_2Br_3(OH)_5$ . The methods adopted for its preparation (by the action of bromine water) and for the preparation of the analogous chloro-compound\* (potassium chlorate and hydrochloric acid or chlorine in hydrochloric acid) are such as would readily permit of oxidation occurring simultaneously with halogenation, and the yields are very poor in both cases. The suggestion that the lower-melting bromo-compound is not a normal bromination product of barbaloin is supported indirectly by a number of comparative experiments which we have carried out. We have been unable to prepare the bromo-compound except by the use of bromine water; bromination of barbaloin in acetic acid solution containing sodium acetate yields only the sparingly soluble bromo-compound,  $C_{20}H_{15}O_9Br_3$ , and in chloroform solution a substance resembling this in properties, but having a somewhat higher bromine content, is obtained. The last substance requires further study, but we are of the opinion that it is probably a tetrabromo-derivative.

To facilitate differentiation between these two bromo-derivatives, we suggest that the higher-melting compound,  $C_{20}H_{15}O_9Br_3$ , should be known as *tribromobarbaloin*, and the lower-melting derivative as *tribromonorbarbaloin*.

The only evidence which we have discovered directly at variance with the suggestion now made is the observation of Léger that tribromonorbarbaloin and trichloronorbarbaloin yield tetrabromo- and tetrachloro-aloe-emodin, respectively, on oxidation with sodium peroxide in alkaline solution. This reaction needs further investigation: it probably involves more complex changes than the simple hydrolysis required by Léger's formula. This view is supported by the fact that we have not been able to oxidise either acetyltribromobarbaloin or acetyltribromonorbarbaloin to an anthraquinone derivative with chromic acid.

\* We have prepared this chloro-compound and its composition is  $C_{16}H_{15}O_7Cl_3$ .

It is difficult to determine how far the results of the molecular-weight determinations which Dr. Sugden has kindly carried out on tribromonorbarbaloin pentamethyl ether bear on the present problem. These gave the average value of 844, the calculated molecular weight being 629. As has been mentioned, the substance is amorphous and separates from its acetone solution as a gum; the results of the molecular-weight determinations, however, are very concordant. For the present, we are inclined to regard the results as abnormal and due to association. Tribromobarbaloin itself is too sparingly soluble for molecular-weight determinations, but it is proposed to determine those of suitable derivatives.

If the views now stated are correct, the constitutions of barbaloin and of the other aloins must be more complex than has hitherto been assumed. The experimental investigation is being developed in various directions and it should be mentioned that Dr. A. Robertson is studying the synthesis of glucosides of rhein and of aloe-emodin.

#### EXPERIMENTAL.

The barbaloin used throughout this work was purified by two crystallisations from ethyl alcohol and dried over sulphuric acid. It was free from isobarbaloin.

*Tribromobarbaloin*,  $C_{20}H_{15}O_9Br_3$ .—To a solution of barbaloin (5 g.) in hydrobromic acid ( $d$  1.5; 25 c.c.) cooled to  $0^\circ$ , bromine (8 g.) in hydrobromic acid (25 c.c.) was gradually added. No appreciable rise of temperature took place and after 4 hours the mixture was kept at room temperature for 4 days. The mixture was poured on ice, and the voluminous yellow precipitate (5 g.) separated and dried in air. When this was mixed with hot aqueous alcohol (60%, 50 c.c.), a clear reddish-brown solution was obtained, and this, after being boiled for a few minutes, deposited a fine yellow crystalline solid (the filtrate, *A*, was reserved). The bromo-compound was conveniently purified by extraction with acetone in a Soxhlet apparatus; it then separated from the solution as a bright yellow powder. When slowly heated, the compound decomposed with vigorous evolution of gas at  $291^\circ$  after darkening at  $284^\circ$ ; on rapid heating, it decomposed without previous change at  $296^\circ$ . The compound is anhydrous and does not lose weight at  $110^\circ$  (Found: C, 37.7; H, 3.0; Br, 37.8, 37.6. Calc. for  $C_{20}H_{15}O_9Br_3$ : C, 37.5; H, 2.3; Br, 37.5%).

Tribromobarbaloin is extremely sparingly soluble in all the ordinary organic solvents and insoluble in water. It dissolves in much formic acid or acetic acid and separates slowly from the solutions; under these conditions, it appears to undergo some change, since the melting point falls to  $265^\circ$ . It is readily soluble in mineral

acids, the solution in concentrated sulphuric acid being reddish-yellow and slightly fluorescent. It is not attacked by the latter reagent (50%) when heated for a short time, nor does it undergo any change when heated at  $110^{\circ}$  with a methyl-alcoholic solution of hydrogen bromide (3%) in a sealed tube. It is readily soluble in alkalis, yielding golden-yellow solutions. Its alcoholic solution gives with ferric chloride a deep reddish-brown coloration; this becomes paler on warming and the original deeper colour reappears on cooling.

From the filtrate *A*, a small quantity of tribromonorbarbaloin was deposited on dilution with water.

*Acetyltribromobarbaloin*,  $C_{20}H_9O_3Br_3(OAc)_6$ .—The acetylation of tribromobarbaloin was investigated under various conditions, but a homogeneous product was obtained only by the following method. A solution of the bromo-compound (2 g.) in acetic anhydride (20 c.c.) to which two drops of sulphuric acid had been added was boiled for 2 hours. The cooled reaction mixture was poured into water; the heavy oil which was precipitated slowly solidified. The dried and finely powdered solid was purified by means of ligroin (b. p.  $60-80^{\circ}$ ), from which it separated as an almost colourless powder; this was not definitely crystalline. It softened at  $173^{\circ}$  and melted at  $185-187^{\circ}$  to a yellow resin (Found: C, 43.4; H, 3.5; Br, 26.4.  $C_{32}H_{27}O_{15}Br_3$  requires C, 43.1; H, 3.0; Br, 26.9%).

*Acetyltribromobarbaloin* is readily soluble in all the ordinary organic solvents with the exception of ligroin and cyclohexane. It is readily attacked by chromic acid in acetic acid-acetic anhydride solution, yielding an amorphous powder which is insoluble in alkali and has not been purified.

*Tribromobarbaloin Pentamethyl Ether*.—Tribromobarbaloin in acetone was treated with potassium hydroxide solution (20%) and a large excess of methyl sulphate. The colourless oil that separated was converted into a flocculent solid when poured into water. The dried solid was triturated with ether, which left undissolved any partly methylated material; on evaporation, the filtered extract gave the methyl ether as a gum. In two experiments a solid was obtained which crystallised in well-defined prisms; it was very sparingly soluble in ether and apparently free from halogen, but it was not obtained in quantity sufficient for identification.

The *pentamethyl ether* separated as a colourless powder, m. p.  $128-130^{\circ}$ , when water was added to a solution in methyl alcohol-acetone [Found: C, 43.0; H, 4.0; Br, 33.3; OMe, 22.9.  $C_{28}H_{27}O_9Br_3$  requires C, 43.1; H, 3.7; Br, 33.2; (OMe)<sub>5</sub>, 21.4%]. It was somewhat sparingly soluble in methyl alcohol and insoluble in ligroin and water, but readily soluble in ether, ethyl alcohol,

acetone, and ethyl acetate. It was only very slowly attacked by potassium permanganate in hot acetone solution.

*Acetyltribromobarbaloin Pentamethyl Ether*.—When a solution of the preceding ether was treated with acetyl chloride, and the excess of acid chloride removed, the product obtained could not be freed from a red substance which was also formed. A pure product was, however, obtained by using acetic anhydride containing a few drops of pyridine. The *acetyl* derivative, a colourless powder, was purified by precipitation from its solution in methyl alcohol by water. It had m. p. 102—105° after softening at 90° and was readily soluble in all organic solvents except ligroin (Found: C, 44.1; H, 4.1; Br, 31.4; Ac, 6.4.  $C_{28}H_{29}O_{10}Br_3$  requires C, 43.9; H, 3.8; Br, 31.4; Ac, 5.6%).

*Tribromonorbarbaloin*,  $C_{16}H_{15}O_7Br_3$ .—This was prepared by the bromination of barbaloin with bromine water in the manner described in the literature. After crystallising from alcohol and drying under reduced pressure, it had m. p. 193—194°, sintering at 188° and decomposing at 223° (Found: Br, 42.6. Calc.: Br, 42.9%). It can be recovered unchanged from its yellow solutions in alkalis on acidification.

*Acetylation of Tribromonorbarbaloin*.—Tribromotetra-acetylnorbarbaloin,  $C_{16}H_{11}O_3Br_3(OAc)_4$ , was obtained when tribromonorbarbaloin was acetylated with acetyl chloride. After crystallising from aqueous alcohol (70%), it had m. p. 137—139° (Found: Br, 32.5; Ac, 24.0. Calc.: Br, 33.0; 4Ac, 23.7%). It was insoluble in cold alkalis, but was hydrolysed to the parent bromo-compound by alcoholic sulphuric acid. It yielded an amorphous, dark brown powder when oxidised with chromic acid in acetic acid-acetic anhydride solution.

*Tribromopenta-acetylnorbarbaloin*,  $C_{16}H_{10}O_2Br_3(OAc)_5$ , was obtained when tribromonorbarbaloin was acetylated with acetic anhydride in the presence of sulphuric acid. It was sparingly soluble in cold aqueous alcohol (60%) and readily soluble in hot aqueous alcohol; from this solution it was deposited as an amorphous, granular, yellow powder, m. p. 139—140°, softening at 128° (Found: C, 40.5; H, 3.0; Br, 31.0.  $C_{26}H_{25}O_{12}Br_3$  requires C, 40.6; H, 3.2; Br, 31.2%).

*Tribromonorbarbaloin Pentamethyl Ether*,  $C_{16}H_{10}O_2Br_3(OMe)_5$ .—Tribromonorbarbaloin was fully methylated only after two treatments with methyl sulphate and alkali in acetone solution. The *ether*, which separated as a colourless powder, m. p. 112—113° after softening at 101°, was readily soluble in organic solvents and was purified by the careful addition of water to its solution in acetic acid. The white powder, m. p. 115—116°, obtained became yellow

on exposure to air. It was stable to potassium permanganate in acetone solution. Two distinct preparations were analysed [Found : C, 39.5, 40.1; H, 3.6, 3.9; Br, 38.6, 37.8; OMe, 21.4.  $C_{21}H_{25}O_7Br_3$  requires C, 40.0; H, 4.0; Br, 38.1; (OMe)<sub>5</sub>, 24.6%].

The methyl ether cannot be reduced with zinc dust in the cold, but, on warming in acetic acid solution, bromine is eliminated, the product being an amorphous solid which has not been purified. The ether is insoluble in alkali, gives with nitric acid an intense purple-violet coloration and with sulphuric acid a deep purple, is somewhat readily attacked by potassium permanganate in acetone solution, and when oxidised with lead peroxide yields a substance which gives a green colour with sulphuric acid.

We desire to express our indebtedness to Messrs. Burroughs, Wellcome and Co. and to Dr. H. A. D. Jowett for generous gifts of material which have made this investigation possible. To Professor R. Robinson, F.R.S., we are also greatly indebted for the considerable help and suggestive criticism which he has freely given during the progress of the work. Part of the expense of the investigation has been met out of a grant from the Government Grant Committee of the Royal Society, which we gratefully acknowledge.

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## LXXIX.—*The Action of Nitric Acid on Some Metals.*

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INVESTIGATION of the kinetics of the dissolution of metals in acids with evolution of hydrogen (compare Centnerszwer, *Z. physikal. Chem.*, 1929, **A**, **141**, 297) has shown that the reactions involved are more complex than the simple electronic exchange often represented in text-books of electrochemistry. When nitric acid is the reagent, the numerous reduction products afford even greater complexity of reaction and the matter appears to have received less attention, although it is of technical importance.

Previous investigators (Acworth and Armstrong, *J.*, 1877, **31**, 60; Freer and Higley, *Amer. Chem. J.*, 1899, **21**, 377) have studied primarily the gaseous products of reduction of nitric acid at various concentrations by different metals (see summary by Bancroft, *J. Physical Chem.*, 1924, **28**, 474). Divers (*J.*, 1883, **43**, 465) classified metals into two groups in respect of their action on nitric acid: copper, mercury, silver, and bismuth produce water, nitrous

acid, and the nitrate of the metal, whilst zinc, cadmium, magnesium, aluminium, lead, iron, and the alkali metals do not yield nitrous acid, but give ammonia and generally also hydroxylamine. One of these groups includes metals which do not disengage hydrogen from hydrochloric acid, and the other comprises metals which do so.

For many years two rival theories have existed. According to one view, the first product of reaction of a metal such as copper with nitric acid is hydrogen, which, however, does not appear as such, but, being in the nascent state, reduces the nitric acid to a variety of reduction products depending on the conditions of reaction. In support of this, it is urged that free hydrogen is obtained when magnesium acts on very dilute nitric acid. Acworth and Armstrong (*loc. cit.*) incline to this view and write  $\text{Cu} + 2\text{HNO}_3 = \text{Cu}(\text{NO}_3)_2 + 2\text{H}$  to represent the first stage. Supporters of the other view regard the metal itself as the reducing agent and deny the production of hydrogen.

In the present paper a study has been made of the influence of rotation on the rate of reaction of some metals with nitric acid, and the results show that these metals fall definitely into two groups, the members of which are respectively electronegative and electropositive to hydrogen: the hydrogen theory probably holds for the first group and the oxidation theory for the second.

#### EXPERIMENTAL.

The experiments described below were suggested by the accidental observation that some nitric acid in which an immersed copper sheet had been rotating for some hours had not acquired a blue colour. It was then found that Veley (*J. Soc. Chem. Ind.*, 1889, 8, 858; *Phil. Trans.*, 1891, A, 182, 279) had already observed that a rolling sphere of copper dissolved more slowly in nitric acid than a stationary sphere, and that the cause of the phenomenon was the removal of nitrous acid, which acts as an autocatalyst, from the surface of the dissolving metal.

In the following experiments, metal sheet 1 mm. thick was cut into strips 7 cm. long, which were 1 cm. wide over a length of 4 cm. and 0.6 cm. wide over the remaining 3 cm. A length of 5 cm. of the strip was immersed in the acid, so that the immersed portion comprised all the 1 cm.-wide part and 1 cm. of the 0.6 cm.-wide part. By means of a small hole bored at the upper end, the strip was screwed to a nickel rod which could be rotated at speeds up to 3000 r.p.m. by means of an electric motor. The reason for narrowing the upper portion of the strip was to reduce the area in contact with the liquid line where preferential corrosion occurs (Hedges, *J.*, 1926, 831). The method is somewhat crude, but is probably

better than the more usual way of immersing the support in the acid and covering all except the desired portion with wax or some other protective coating : small quantities of such materials may exert a profound influence on the reaction (compare Hedges and Myers, J., 1924, **125**, 604). All the nitric acid used was freed from nitrous acid by being warmed to 30° whilst a vigorous stream of air bubbles passed through it. The metals were cleaned by etching with nitric acid. The experiments were conducted in a thermostat at 30° and the loss of weight of the metal after 1 hour's immersion was determined. In general, it was found that repetitions of the same experiment gave results agreeing within 3—4%, although occasionally larger discrepancies appeared. The figures given in the tables represent the mean of two results differing by not more than 5%. This degree of concordance is quite sufficient, since the changes studied are of a much higher order.

*Influence of Speed of Rotation on Rate of Dissolution.*—(1) *Copper in 25% \* nitric acid.*

Speed (r.p.m.) ...	0	80	100	180	360	450
Loss of wt. (g.) ...	1.312	0.259	0.131	0.079	0.014	0.003

The velocity of dissolution is greatly reduced by quite moderate rates of rotation, and at 450 r.p.m. has become exceedingly slow. The results indicate that the velocity of dissolution of copper in pure nitric acid is very low and that some product of the reaction which normally accumulates at the surface of the metal is an active catalyst. In the process of rotation, this catalyst is washed away from the surface as fast as it is formed, and consequently the reaction is slower than in the stationary state. If this explanation holds, it should be possible to increase greatly the velocity of dissolution of a rotating copper sheet by direct addition of the supposed catalytic reaction product to the nitric acid solution. For this purpose, experiments were conducted on the effect of adding nitrous acid (in the form of sodium nitrite) and copper nitrate at constant speed of rotation of the copper. The results are given below.

*Effect of adding sodium nitrite (constant speed 450 r.p.m.).*

Amt. added, % .....	0	0.1	0.5
Loss of wt. (g.) .....	0.003	0.171	0.622

*Effect of adding copper nitrate (constant speed 360 r.p.m.).*

Amt. added, % .....	0	0.2	1.0	10
Loss of wt. (g.) .....	0.014	0.004	0.004	0.007

Evidently, in agreement with Veley's conclusions (*loc. cit.*), nitrous acid is the reaction product responsible for the high speed of reaction in the stationary state. Copper nitrate, even in relatively

\* Percentages relate to acid of *d* 1.42 (by vol.).

large amounts, did not increase the velocity of reaction, an observation which is contrary to that of Rennie, Higgin, and Cooke (J., 1908, 93, 1162), who state that the reaction is greatly accelerated by copper nitrate. These authors did not rotate the metal but stirred the liquid—an inefficient means of replenishing the layer of liquid in contact with the solid.

(2) *Silver in 25% nitric acid.*

	Stationary.	At 450 r.p.m.	At 450 r.p.m., with 1% of NaNO <sub>2</sub> .
Loss of wt. (g.) .....	1.174	0.000	1.187

Rotation of silver at 450 r.p.m. inhibited dissolution by nitric acid completely, and the solution gave no reaction for silver ions when tested with hydrochloric acid. Addition of 1% of sodium nitrite to the rotating system brought the velocity of dissolution to practically the same value as that of stationary silver.

(3) *Tin in 25% nitric acid.*

	Stationary.	At 450 r.p.m.	Stationary with 1% of NaNO <sub>2</sub> .
Loss of wt. (g.) .....	0.270	0.390	0.114

(4) *Zinc in 10% nitric acid.*

	Stationary.	At 450 r.p.m.
Loss of wt. (g.) .....	1.476	3.222

(5) *Magnesium in 5% nitric acid.*

	Stationary.	At 450 r.p.m.	Stationary with 0.5% of NaNO <sub>2</sub> .
Loss of wt. (g.) .....	0.270	0.480	0.240

The results for tin, zinc, and magnesium show a striking difference from those for copper and silver. The rate of dissolution is *increased* when the metal is rotated, and nitrous acid has no accelerating effect; indeed, substitution of nitrous acid for some of the nitric acid reduces the velocity of dissolution of tin.

*Further Examination of the Copper-Nitric Acid System.*—Veley (*loc. cit.*) found that copper did not dissolve in dilute nitric acid containing a substance such as urea which could destroy the nitrous acid as fast as it is formed. The author's experiments confirmed this observation, but also showed that copper dissolves readily in concentrated nitric acid even when saturated with urea, and that dissolution started in the dilute solutions on gentle warming. In the following experiments, concentrated nitric acid (*d* 1.42) was saturated with urea, and the solution diluted with distilled water in the proportion stated; 5 c.c. of the mixture were put into a test-tube immersed in a large beaker containing water, the temperature



of which was raised by  $1^{\circ}$  per minute. A small piece of copper was dropped into the mixture at  $25^{\circ}$ .

$\text{HNO}_3\text{-CH}_4\text{ON}_2$ mixture, c.c.	$\text{H}_2\text{O}$ , c.c.	Result.
5	—	Immediate dissolution.
4	1	" "
3	2	Dissolution after 2—3 secs.
2	3	Dissolution after 5 secs.; reaction stopped by shaking tube.
1.5	3.5	No reaction at $25^{\circ}$ ; reaction starts at $27^{\circ}$ , and ceases if temp. is decreased.
1	4	As in preceding case, but $37^{\circ}$ is now the critical temperature.

Similar phenomena were observed when hydrogen peroxide or potassium permanganate was added to remove the nitrous acid, and the results indicate that these reagents are in general less effective than rapid stirring in removing the nitrous acid. In the more concentrated solutions at  $25^{\circ}$ , and in dilute solutions of nitric acid at higher temperatures, nitrous acid is produced by the reducing action of copper at a rate greater than that at which urea or hydrogen peroxide can react with it.

This conclusion made it of interest to determine whether a considerably higher speed of rotation could prevent the dissolution of copper by concentrated nitric acid ( $d$  1.42), and it was found that, although the reaction could not be stopped, its velocity was greatly reduced. For this purpose, a piece of copper foil 1 cm.  $\times$  1 cm.  $\times$  0.01 cm. was pierced and suspended by a glass hook which was lowered into an empty beaker and rotated at 2000 r.p.m. Concentrated nitric acid was then poured into the beaker. At rest, a piece of metal of these dimensions dissolved completely in the acid in less than 30 seconds, but when it was rotated at 2000 r.p.m., after an interval of about 6 mins. (during which the solution developed a green colour) the foil always left the hook, being still partly undissolved. The piece of copper left had a black skin and appeared to be passive, dissolving in the acid extremely slowly even when at rest. Some specimens were not completely dissolved after 60 mins. An interesting behaviour was observed when one of these specimens was removed from the nitric acid and allowed to drain. After a few seconds, momentary effervescence appeared on the surface, the black film disappeared, and the metal was found to have lost its passivity towards nitric acid. This behaviour resembles exactly that of electrolytic iron which has been rendered passive by concentrated nitric acid, removed, and allowed to drain (Evans, J., 1927, 1020). Evans considers that the phenomenon is caused by the tendency of the protective film to leave the metal-liquid interface and collect at the air-liquid interface.

These results suggest that, in the absence of nitrous acid, nitric acid produces a protective oxide film on copper, which is thus rendered passive in a similar way to the well-known action of concentrated nitric acid on iron. The black film mentioned above resembled that observed by the author on copper which had been rendered passive by immersion in concentrated nitric acid at  $-11^{\circ}$  (J., 1928, 975).

*The Anodic Dissolution of Copper in Nitric Acid.*—The dissolution of a copper anode in nitric acid is also affected greatly by the presence of nitrous acid. For example, during passage of a current of 50 milliamps. for 1 hour, a stationary anode lost 0.790 g. of copper, but when rotated at 400 r.p.m. it lost only 0.270 g.; when 2% of sodium nitrite was added, however, it lost 1.408 g.

In the following experiments, a rotating anode of the type previously described (J., 1927, 1028) was used, the cathode was of platinum foil, and the anode and cathode compartments were separated by means of a porous pot. The experiments were conducted in 25% nitric acid at  $30^{\circ}$ . The following table shows the loss of weight of the anode both when stationary and when rotated at 400 r.p.m. at various current densities. The last column gives the loss of weight to be expected in accordance with Faraday's law.

Current, milliamps.	Loss of weight, g.		
	Stationary.	At 400 r.p.m.	Calc.
0	1.312	0.01	0.000
25	1.158	0.096	0.592
50	0.790	0.270	1.185
100	1.000	0.280	2.369
500	1.314	0.586	11.848

It will be observed that in every case the rotating anode dissolves more slowly than the stationary anode, although at the higher current densities the difference is relatively less. At 25 milliamps. the loss is about twice as great as that calculated from Faraday's law, which means that much of the dissolution is controlled by local short-circuited electrolytic cells in the metal, the electrical energy of which is not registered on the external circuit. At higher current densities the loss is much less than that required by this law, the discrepancy increasing with the intensity of the current. In these cases, evolution of gas at the anode was observed, so that only a portion of the electrical energy is involved in the formation of cupric ions. Thus it appears that copper readily becomes passive, though incompletely so, under anodic polarisation, and the more readily so in absence of nitrous acid. At the end of the experiments, these electrodes had a black or grey film over their surface.

*Difference of Potential between Stationary and Rotating Copper Anodes.*—The difference of electropotential between the electrodes and a reference normal calomel electrode was measured by a static method, the measuring instrument being a string electrometer. The method was similar to that already described (J., 1927, 1077). The measurements were carried out both with stationary and with rotating (400 r.p.m.) electrodes, over the *C.D.* range 5–50 milliamps./cm<sup>2</sup>, and throughout this range the rotating electrode was positive (noble) to the stationary electrode by 0.16 volt. This result is in the direction to be expected from the presence of an oxide film on the rotating electrode.

### *Discussion.*

The metals investigated fall into two classes accordingly as the velocity of dissolution in nitric acid is increased or decreased by rotation. The presence of nitrous acid does not appreciably affect the rate of dissolution of members of the first group, but it accelerates very greatly that of metals of the second group. These groups are coincident with those of Divers (*loc. cit.*), who used as a basis of classification the nature of the reduction products. Members of the first group are electronegative to hydrogen, and those of the second group are electropositive.

The electronegative metals can normally displace hydrogen from acids and their behaviour provides no reason to doubt that they initially displace hydrogen from nitric acid; the hydrogen reduces the nitric acid to oxides of nitrogen and sometimes to ammonia and hydroxylamine. When the nitric acid is extremely dilute, hydrogen can be obtained in the free state by the dissolution of magnesium.

On the other hand, there is no *a priori* reason why the second group, consisting of electropositive metals, should displace hydrogen from nitric acid, since they do not do so from other acids.

The passivity phenomena observed when copper is rotated in concentrated nitric acid, the observations on the anodic dissolution of copper, the difference of potential between stationary and rotating copper electrodes, and the formation of visible black films on the copper all suggest that an oxide film is formed on copper by the action of nitric acid. There is also the fact that nitrous acid is produced and accelerates the reaction; part of this acid reacts with the copper oxide, for, particularly in the early stages, the soluble product contains green copper nitrite as well as the blue copper nitrate, and part of it is decomposed to oxides of nitrogen, which are the gases evolved.

The suggested reactions may be represented thus :

- (1)  $\text{Cu} + \text{HNO}_3 = \text{CuO} + \text{HNO}_2$ ;
- (2) (a)  $\text{CuO} + 2\text{HNO}_2 = \text{Cu}(\text{NO}_2)_2 + \text{H}_2\text{O}$ ;
- (b)  $\text{CuO} + 2\text{HNO}_3 = \text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{O}$ ;
- (3)  $\text{Cu}(\text{NO}_2)_2 + 2\text{HNO}_3 = \text{Cu}(\text{NO}_3)_2 + 2\text{HNO}_2$ ;
- (4) (a)  $3\text{HNO}_2 = \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$ ;
- (b)  $\text{HNO}_2 + \text{HNO}_3 = 2\text{NO}_2 + \text{H}_2\text{O}$ .

In dilute acid 4 (a) gives nitric oxide as the main product, whilst in concentrated acid 4 (b) preponderates and the main gaseous product is nitrogen peroxide : a mixture is usually produced.

If, by rotation or by addition of such a substance as urea, the nitrous acid formed in (1) can be removed continuously, the metal becomes covered with a film of copper oxide and dissolves only slowly. Nitrous acid may be said to "activate" the copper, perhaps in the same way that chlorine ions activate passive iron. In any case, the mechanism of this process of activation is not clear, but in some way the activating agent appears to loosen the protective film.

The theory outlined above supposes that cupric oxide can afford a sufficient degree of protection to the underlying metal, although ordinarily this substance is readily soluble in nitric acid. To test this point, some rough experiments were carried out on the rate of dissolution in nitric acid of samples of cupric oxide prepared in different ways. The method was to add 1 g. of the powdered oxide to 100 c.c. of 25% nitric acid, which was efficiently stirred at a constant rate by means of a glass stirrer, and to note the time taken for complete dissolution. An ordinary commercial sample dissolved in 3 mins. A sample prepared from copper sulphate by precipitation with sodium hydroxide and ignition of the residue was completely dissolved in 5 mins. A sample prepared by igniting cupric nitrate was incompletely dissolved after 60 mins. It is possible, therefore, for a form of cupric oxide to be sufficiently resistant to nitric acid to form a poorly protective film of the type required. The fact that the films are sufficiently thick to be easily visible is an indication of the low degree of protection afforded compared with that of the oxide film on passive iron. As fast as the relatively porous cupric oxide film is dissolved it is repaired by the nitric acid.

Thus, nitric acid appears to oxidise copper and silver superficially, causing them to become passive, and the action of nitrous acid, both on the ordinary chemical reaction and on the anodic dissolution, may be described as one of "activation," though in what way it removes the protective film is not at present understood.

Although in the dissolution of electronegative metals in dilute nitric acid the displacement of hydrogen appears to be the first reaction, in concentrated acid the oxidation reaction may preponderate. Tin and iron form two excellent illustrations. Tin dissolves in dilute nitric acid, giving stannous nitrate, and the hydrogen reduces the nitric acid mainly to ammonia; in concentrated nitric acid a hydrated stannic oxide is produced, but has not the requisite physical properties for forming a good protective coating. Similarly, iron dissolves readily in dilute nitric acid, but in concentrated nitric acid receives a thin film of ferric oxide which protects it from further action, and the iron is said to be passive.

*Summary.*

The rate of dissolution of copper and of silver in nitric acid is decreased and can be almost prevented by rotation of the metal: the cause of this phenomenon is that nitrous acid (one of the products of reaction) is not allowed to accumulate at the metal surface. Direct addition of nitrous acid causes the rotating metal to dissolve rapidly. On the other hand, tin, zinc, and magnesium dissolve more rapidly in dilute nitric acid when rotated, and nitrous acid has no accelerating effect. Copper which has been rotated rapidly in concentrated nitric acid acquires a black film and becomes "passive" towards nitric acid, dissolving slowly even when subsequently at rest: it shows passivity phenomena in other respects. A copper anode also dissolves more slowly in nitric acid when rotated than when at rest for a given current density, but addition of nitrous acid accelerates the rate of dissolution. A rotating copper anode is electropositive by 0.16 volt to a stationary copper anode. The results suggest that the first action of nitric acid on copper or silver is one of oxidation, forming an oxide film which prevents further rapid attack, *i.e.*, the metal becomes passive; nitrous acid acts as an activating agent. The initial product of reaction of tin, zinc, or magnesium with dilute nitric acid is probably hydrogen. The results are discussed in relation to the passivity of iron.

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LXXX.—*The Measurement of the Dielectric Constants of Organic Liquids.*

By ALFRED OWENS BALL.

THE interest aroused within recent years in the measurement of dielectric constants of liquids has been caused not only by the extension of accurate conductivity measurements to non-aqueous solutions and the development of the Debye-Hückel theory of strong electrolytes, but also by the use of the values of this property for determining dipole moments. In both cases a demand has been created for simple and rapid routine methods of proved accuracy and for trustworthy data relating to a few standard liquids for calibration purposes. These requirements can be satisfied in the case of good insulators, for which the heterodyne method is probably the best and simplest (Herweg, *Verh. deut. physikal. Ges.*, 1919, 21, 272; *Z. Physik*, 1920, 3, 36; Whiddington, *Proc. Camb. Phil. Soc.*, 1921, 20, 445; Grützmacher, *Z. Physik*, 1924, 28, 342) and for which benzene may be used for calibration purposes on the basis of the work of Hartshorn (*Proc. Roy. Soc.*, 1929, A, 123, 664). In the case of liquids which are not good insulators, however, the author is of the opinion that, although the resonance methods (including, as a special type, the heterodyne method) are simpler in operation, they are more likely to be affected by small and unsuspected errors due to conductivity than are the alternating-current bridge methods. Also, there appears to be no liquid possessing any appreciable conductivity for which really concordant results have been recorded, and the discrepancies may be attributable to any of the following causes: (1) experimental errors of the operator; (2) errors inherent in the method employed, these errors being possibly a function of the conductivity and of the frequency at which the determination is made; and (3) a real variation in the dielectric constant with the frequency.

The work described in the present paper was originally commenced in order to determine the dielectric constants of a few organic liquids with a view to correlation with conductivity measurements made in these laboratories (Philip and Oakley, on nitromethane, *J.*, 1924, 125, 1189; Martin, on benzonitrile, *J.*, 1928, 3270). In view of the considerations outlined above, however, it was decided to attempt to determine the dielectric constants of a few standard liquids over a range of frequency and temperature by means of an alternating-current bridge. This method has the further advantage over the resonance method that it is more convenient for absolute measurements when no calibrating liquid is

available (see p. 582). It was also intended to use these same liquids to compare the results afforded by the bridge method and one or more resonance methods at a constant high frequency. The results of using this method at audible frequencies are now recorded.

### *Alternating-current Bridge Systems.*

An alternating-current bridge may be used to determine the impedance operator of a system in the same manner as a direct-current bridge is employed to determine resistance. A theoretically perfect capacity of magnitude  $C$  has an impedance operator  $-j/\omega C$ , where  $j = \sqrt{-1}$ , and if an alternating potential is applied to it, the current vector will lead the voltage vector by  $\pi/2$ . In practice, however, owing to conductance of current through the medium, or absorption, or resistance of plates and contacts, the angle of lead is less, and the impedance operator cannot be represented in this way.

It is very important to emphasise the equivalence of capacity and resistance circuits to an imperfect condenser. The condenser is determined as its impedance operator, that is to say (in theory), as the quotient of the vector of the current carried by the vector of the voltage applied. Let the numerical value so found be  $a + bj$ . Now a capacity  $C_1$  and a resistance  $R_1$  in series have an impedance operator  $R_1 + \frac{1}{j\omega C_1}$ , and if this be put identically equal to the value  $a + bj$ , the two resultant expressions obtained by equating the real and the imaginary terms can be solved for  $C_1$  and  $R_1$ . Further, a capacity  $C_2$  and a resistance  $R_2$  in parallel have an impedance operator  $\frac{1}{1/R_2 + j\omega C_2}$ , and again unique values of  $C_2$  and  $R_2$  can be found which will make this expression assume the value  $a + bj$ . On the other hand, however, the impedance operator of a circuit consisting of a capacity and shunt resistance together with another resistance in series will involve three constants, and any number of solutions may therefore be obtained which will give it the value  $a + bj$ . That is to say, if a given imperfect condenser really consists of a capacity with resistances both in series and in parallel, it is impossible to determine the capacity simply by measuring the impedance operator of the whole system. Such a case as this might be imagined as one in which there was a conductance leak between the plates of the condenser, together with a terminal or contact resistance. The important point is that, from the impedance operator of a condenser, it is only possible to calculate values of two capacities, such that either the one, together with a resistance in parallel, or the other, with a resistance in series, will have an impedance operator identical with

that of the condenser in question. It is customary to term the resistances in these two cases the "equivalent shunt resistance" and the "equivalent series resistance" respectively, but it must not be forgotten that the corresponding capacity values are also merely "equivalent," and that neither can definitely be said to be the true capacity involved unless information is available regarding the internal physical structure of the system.

It is important, therefore, to consider the type of condenser to be measured, and to ascertain whether it approximates sufficiently closely to one or other of the above systems for the capacity values deduced thereby to be valid. Now, the great majority of organic liquids possess, even when highly purified, an appreciable conductivity, and the most serious imperfection in the condenser is the consequent (relatively) low shunt resistance. If, then, there is any further resistance in series, the equivalent shunt capacity of the system will not be equal to the actual capacity, the error involved being easily calculated in the following manner.

Suppose the condenser consists of a capacity  $C_1$  in parallel with a resistance  $R_1$ , both being in series with another resistance  $R_2$ .

Then its impedance operator will be  $Z_1 = R_2 + 1 / \left( \frac{1}{R_1} + j\omega C_1 \right)$ .

This condenser is now to be assumed equivalent to a system consisting of capacity and resistance in parallel. Let this capacity and resistance be  $C$  and  $R$  respectively, in which case the impedance operator is  $Z = 1 / \left( \frac{1}{R} + j\omega C \right)$ . Since the two systems are equivalent,

$Z$  and  $Z_1$  must have the same value, and hence after equating the two expressions the following solutions are obtained for the equivalent shunt resistance  $R$  and the equivalent shunt capacity  $C$ :

$$R = \frac{(R_1 + R_2)^2 + \omega^2 C_1^2 R_1^2 R_2^2}{(R_1 + R_2) + \omega^2 C_1^2 R_1^2 R_2^2}$$

$$C = \frac{C_1 R_1^2}{(R_1 + R_2)^2 + \omega^2 C_1^2 R_1^2 R_2^2}$$

Now, the dimensions of the condensers used in this work are such that, with a representative liquid, the capacity and shunt resistance are of the order of 0.001 microfarad and  $10^4$  ohms respectively. Under these conditions, and for a frequency of 1000, the term  $\omega^2 C_1^2 R_1^2 R_2^2$  will be negligible compared with  $(R_1 + R_2)^2$  provided that  $R_2$  is small, and in that case

$$C = C_1 \left( \frac{R_1}{R_1 + R_2} \right)^2 = C_1 \left( 1 - \frac{2R_2}{R_1} \right) \text{ (approx.)}$$

From this it appears that it is justifiable to regard the experi-



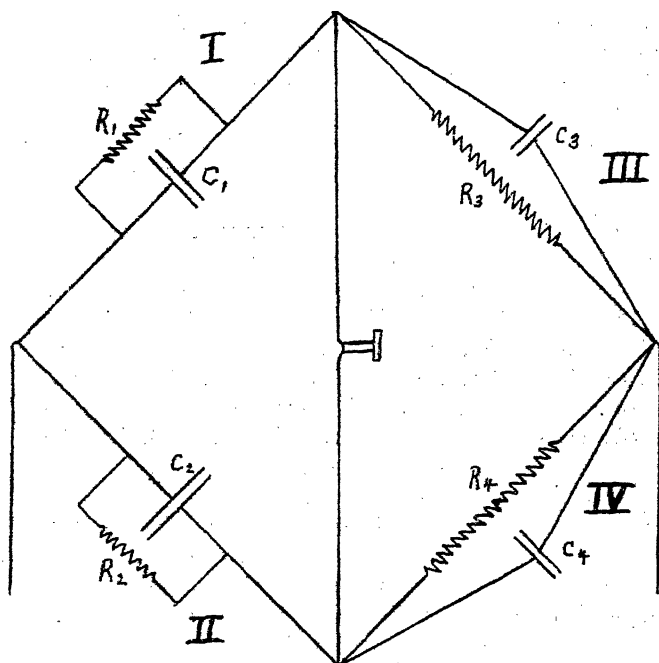
mental condenser as consisting of a capacity and a resistance in parallel, but only provided that the internal resistance of plates and contacts, together with the resistance effects due to absorption, is sufficiently small. It is shown later (p. 588) that this condition is satisfied by the dielectric containers in use.

Returning now to alternating-current bridge measurements, it is seen that a method is required that will permit of the measurement of a capacity of the order of 0.001 microfarad when shunted by a resistance varying down to less than 10,000 ohms, i.e., a condenser of very large loss angle. The simplest way of determining a pure capacity by an alternating-current bridge is that of De Sautig, adapted for alternating current by Wien (*Ann. Physik*, 1891, **44**, 697), in which two condensers are balanced against two resistances. But in this system no allowance is made for the difference in power factor of the condensers being compared, and, in consequence, the minima obtained are very flat, and indeed in many cases impossible of detection.

Of the methods that have been suggested to correct for this difference in power factor, it is only proposed to consider the parallel resistance method, first elaborated by Nernst (*Z. physikal. Chem.*, 1894, **14**, 622) and Turner (*ibid.*, 1900, **35**, 385), and subsequently used by Philip (*ibid.*, 1897, **24**, 18), Linebarger (*ibid.*, 1896, **20**, 131), Tangl (*Ann. Physik*, 1903, **10**, 748, 1903), Richards and Shipley (*J. Amer. Chem. Soc.*, 1919, **41**, 2002), King and Patrick (*ibid.*, 1921, **43**, 1835), Grimm and Patrick (*ibid.*, 1923, **45**, 2794), and Harris (J., 1925, **127**, 1049). The procedure is usually to introduce the experimental condenser into the first arm of the bridge and then to restore balance by adjustment of a standard condenser and a compensating shunt resistance in the second arm. It must be emphasised, however, that in the case of condensers of very large loss angle this method is subject to certain inaccuracies, because the full bridge system is that shown in Fig. 1. The capacities  $C_3$  and  $C_4$  across the ratio arms III and IV are due (i) to the residual capacity of the component resistances and their connecting leads, and (ii) to the earth capacities from the detector points if the Monasch earth point is used (*Electrician*, 1907, **59**, 416, 460, 504). Now the balance equations for this system are  $C_1R_3 = C_2R_4 + R_3R_4(C_3/R_2 - C_4/R_1)$  and  $1/R_1R_4 - 1/R_2R_3 = \omega^2(C_1C_4 - C_2C_3)$ ; if it is balanced first with  $R_1$  and  $R_2$  large,  $C_1R_3 = C_2R_4$ ; and if the experimental condenser  $C_x$  is then introduced across arm I and the new reading of  $C_1$  is  $C_1'$ , then  $(C_1' + C_x)R_3 = C_2R_4 + R_3R_4(C_3/R_2 - C_4/R_1)$ , and therefore  $C_x = (C_1 - C_1') + R_4(C_3/R_2 - C_4/R_1)$ . At balance,  $R_1$  and  $R_2$  are approximately equal, and in the bridge used  $R_3 = R_4 = 1000$  ohms.

In the extreme case when  $R_1$  approaches the value  $10^4$ , it is evident that the measured value of  $C_x$  will be in error by one-tenth of the difference  $C_3 - C_4$ , and if the earth capacities from the detector points are involved in this quantity by the use of the Monasch device, the error may be considerable. But even if the Wagner earth point is used, it is impossible to be absolutely certain that the residuals in the ratio arms III and IV are equal, and, moreover, inductance effects constitute an equally likely source of error. It

FIG. 1.



is advisable, therefore, that  $R_1$  and  $R_2$  should be maintained constant during the course of a measurement, and the condenser completely determined by substitution in arm I of the bridge. That is to say, a system is set up such that arm I consists of a capacity and resistance in parallel, the capacity being greater and the resistance less than the equivalent shunt capacity and resistance of the experimental condenser, which is then inserted across this arm, and balance is restored by adjustment of the capacity and resistance in this same arm only.

It should be noted also that the Monasch earth device is quite definitely an approximation, and is valid only when the impedance

of the capacity arms I and II is large compared with that of the ratio arms III and IV. Since this condition does not hold in the present work, the Wagner method of correcting for earth capacities has been used throughout (*Elekt. Z.*, 1911, 32, 1001; 1912, 33, 635).

#### *The Compensating Resistances.*

The chief requirement of the compensating resistance is that its residual capacity (and inductance) should be constant over the range of operations—which, in the case of the present work, is from a few thousand ohms upwards. Wire resistances of known residuals were not, unfortunately, available, and the Nernst-Turner types of liquid resistance were not entirely satisfactory over the lower part of the range, owing, first, to heating effects of the current, and secondly, to capacity changes which were by no means negligible even when the electrodes were heavily platinised to reduce the polarisation capacity. At first, attempts were made to calibrate for these residuals by means of a platinum-film resistance, but eventually the main substitution was effected by means of a carbon-film resistance, one of the liquid resistances being retained in parallel merely for purposes of fine adjustment. The carbon film used consisted simply of a thick line drawn on a piece of ground glass with an ordinary black-lead pencil, contact being established over any required length of the film by two amalgamated copper wires dipping into small drops of mercury. Provided that the film and mercury contacts are freshly prepared and quite clean, the resistance thus obtained is perfectly definite over a considerable length of time. It is further necessary to provide a distance control for the resistance, and the system used is shown in Fig. 2. A and B are wire electrodes heavily platinised, and C is a solid glass rod controlled from a distance by a cord passing over a pulley. By adjusting the position of A in the narrow tube D the total resistance of the cell can be made large compared with the effective resistance of the whole arm of the bridge with which it is placed in parallel, and thus the movement of the plunger in the wide limb E can be made to afford as fine an adjustment as is required. The electrolyte is the usual solution containing boric acid and mannitol (Magnanini, *Z. physikal. Chem.*, 1890, 6, 58; Nernst, *ibid.*, 1894, 14, 631). This resistance is always in circuit, and the electrode A is not moved during the course of a measurement. It is only necessary, therefore, to ascertain whether the movement of the plunger causes any change in the residual capacity of the system. This was done by rebalancing the bridge a number of times, the setting of the auxiliary liquid resistance being altered very slightly each time over a part of its range for which it was known to have no residual error. The position of the

plunger for balance was thus different each time, but even when the electrode A occupied its minimum position during the test (and hence carried the maximum current) no change in the capacity reading of the bridge could be detected. This determination was made especially because it was thought probable that polarisation

FIG. 2.

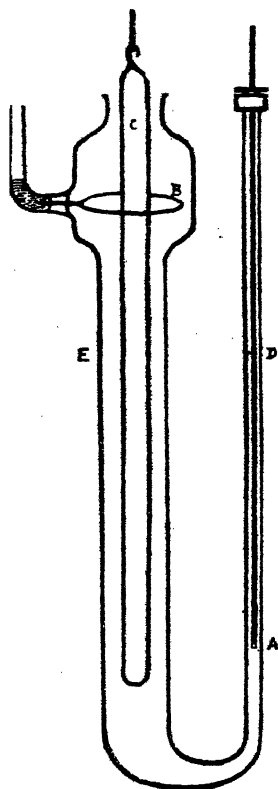
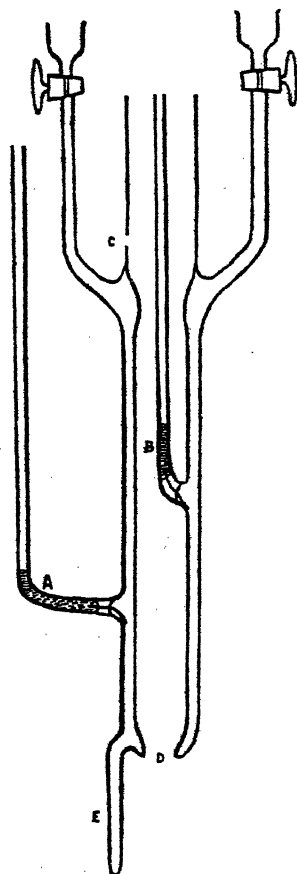


FIG. 3.



capacities might be set up owing to the small area of the wire electrodes.

#### *The Standard Condenser and Measuring Systems.*

As previously shown, the measurement of the capacity of a condenser filled with a liquid of relatively high conductivity is only possible by means of a substitution method, both the capacity and

the resistance being substituted in the same arm of the bridge. It has also been noted already that, since the dielectric constant is a ratio, it is not necessary to know the capacity of the dielectric container in absolute units, and hence the only requirement of the measuring system is that equal intervals on the scale should correspond to equal capacity changes. Since, however, this is an ideal to which practical systems can only be made to approximate, it is necessary that the appropriate calibration corrections be determined, and applied to every reading.

The standard measuring instrument available for the present work was a Sullivan variable air condenser, having a total range of about 1200  $\mu\mu$  farad. The scale was divided into 180° and was fitted with a vernier reading directly to tenths, and permitting a rough estimate of the second decimal place by means of a lens. It may be noted that, except in the case of liquids of high conductivity, the sharpness of the bridge setting always exceeded the accuracy with which the condenser scale could be read.

Now, a convenient value of the air capacity of a condenser of the Sayce and Briscoe type as used was found to be of the order of 50  $\mu\mu$  farad  $\equiv 7^\circ$ , and this could therefore be determined with an accuracy of at most 1%, this error being consequently involved in all subsequent dielectric measurements. Since it was desired to reach an ultimate accuracy of at least 0.2%, it was necessary to use either a larger capacity or a more open scale. The former was found to be impracticable with the type of condenser in use, and a measuring system was therefore set up similar to that suggested by Hartshorn (*Proc. Physical Soc.*, 1924, 36, 399). The standard variable air condenser  $C_1$  was placed in parallel with a fixed mica condenser  $C_2$ , both being in series with another fixed mica condenser  $C_3$ .  $C_2$  and  $C_3$  were made by Sullivans and had nominal capacity values of 0.002 microfarad and 0.00175 microfarad  $\equiv 290^\circ$  and  $250^\circ$  respectively. These condensers were guaranteed constant in capacity and power factor and of very small temperature coefficient, and in use they gave complete satisfaction.

The system constructed in this manner has a much more open scale than the standard condenser alone, but the relation between the capacity of the system and the scale reading of the standard is non-linear. The capacity of the system is  $C = (C_1 + C_2)C_3 / (C_1 + C_2 + C_3)$ , and for a straight-line relationship to hold between  $C$  and  $C_1$  it would be necessary that  $C_1$  should be negligibly small in comparison with  $C_2$  and  $C_3$ , but in this case not only does the net capacity of the system become inconveniently large, but the degree of constancy required of the fixed condensers will be correspondingly greater. It was therefore decided to use the system as described

and to perform the calibration in the following manner. A small constant capacity of about  $2.5^\circ$  was measured over successive portions of the scale of  $C_1$ , the actual scale differences ranging from about  $14^\circ$  to  $20^\circ$ . Each particular scale reading  $C_1$  was then reduced to the corresponding (approximate) value of  $C$  by the formula  $C = 250(C_1 + 290)/(C_1 + 290 + 250)$ , the nominal values of  $C_2$  and  $C_3$  being used, and since the reduced scale differences so obtained were then found to be constant to a first approximation, it was possible to draw up an ordinary calibration curve showing the correction to be applied at any point on the reduced scale. To demonstrate the order of accuracy attainable in this way, a series of 16 measurements was made on the air capacity of one of the dielectric containers. It was found that, excluding one reading (8.335) which was probably due to an error of observation, the values ranged between 8.299 and 8.323, with a mean of 8.310. It is certainly safe to ascribe an error of less than  $0.01^\circ$  to the arithmetic mean, i.e., an error of about 0.1%.

The measuring system as elaborated in this way gave a total capacity variation of about  $25^\circ$  corresponding to the complete range of  $C_1$ . Since the dielectric containers had an air capacity of about  $6-8^\circ$ , it is evident that, for the determination of dielectric constants above 3, the scale had to be extended by the customary device of placing one or more small fixed condensers in parallel with the whole measuring system, so that their capacity could be added to the latter when required. The condensers used each consisted of a small glass tube about 10 cm. long and 1 cm. in diameter sealed off at the lower end and held in position inside a larger tube filled with mercury. Into the inner tube was also placed some mercury (the quantity depending on the magnitude of the capacity required) so that the level was below that in the outer, thus minimising the effect of any slight displacement. A condenser with a glass dielectric in this manner has of course a definite temperature coefficient, and a small power factor: the former was controlled in practice by maintaining the room at a fairly constant temperature and checking the capacity value before and after each series of measurements; the latter was of no importance since it is only the effective shunt capacity of the condenser which enters into consideration.

The method of connexion adopted for these condensers should be noted. The mercury in the outer tube served as a shield, and was kept permanently connected to the screen terminal of the standard condenser, while contact was established between the other terminal and the mercury in the inner tube by a length of quill tubing filled with mercury and having a platinum wire sealed through the lower extremity. The condenser was inserted into

the measuring circuit when required by depressing a copper wire in the quill tubing, and thus, since the shield was permanently in circuit, the *change* of capacity on making contact was maintained constant and independent of any external effects.

The scale of the measuring system as extended in this way was about  $50^\circ$ , thus enabling liquids to be dealt with up to a dielectric constant of about 6, and the question then arose as to the advisability of extending it by more fixed condensers so that it covered the range up to  $\epsilon = 40$ . The accuracy of the results obtainable, however, is governed (see p. 577) by the accuracy with which the air capacity can be determined, and since this is subject to an error of about 0.1%, there is no need to determine any other capacity to a much greater accuracy than this. Now a liquid of dielectric constant 6 will afford a capacity of about  $40^\circ$ , and since such a capacity can be determined by direct comparison with the standard condenser to within  $\pm 0.05^\circ$ , it is evident that there will be no loss of accuracy in determining the liquids of higher dielectric constant in this way. It is necessary, however, to know the numerical relation between the two measuring systems, and this was found in the following manner. If measurements are made on a number of condensers (all having a capacity of about  $40^\circ$ ) with system I, a series of capacity readings  $C_1, C_2, C_3$ , etc., will be obtained which are all proportional to the absolute magnitude of the capacities concerned, the constant of proportionality being  $K$ . Similarly, if the same condensers are measured on system II (i.e., by direct substitution against the standard air condenser) a series of values  $C'_1, C'_2, C'_3$ , etc., will be obtained with a proportionality constant  $K'$ . Then  $C_1/C'_1 = C_2/C'_2 = C_3/C'_3 \dots = K/K'$ ,  $K/K'$  being the conversion factor between the two systems.

Now the error in determining  $C'$  is about 0.1%, and in  $C$  about 0.02%, and the following table gives an indication of the accuracy of the mean value of the ratio  $K/K'$ . The actual capacities measured were the three dielectric containers filled with appropriate liquids as indicated.

TABLE I.

Condenser.	Liquid.	$C$ .	$C'$ .	$K/K'$ .
25°	I CHCl <sub>3</sub>	39.200	40.26	1.0271
	II "	28.128	28.90	1.0276
	III "	37.501	38.56	1.0282
	I CMe <sub>2</sub> Et-OH	49.273	50.63	1.0276
	II "	35.352	36.33	1.0278
	III "	47.164	48.44	1.0271
	II C <sub>6</sub> H <sub>5</sub> Cl	33.723	34.65	1.0275
	III "	44.905	46.15	1.0277
	I CHCl <sub>3</sub>	43.083	44.25	1.0271
0°	I CMe <sub>2</sub> Et-OH	67.949	69.60	(1.0243)
50°	I "	43.304	44.52	1.0280
				Mean 1.0276

The discrepancy observed for condenser I filled with dimethyl-ethyl carbinol at  $0^\circ$  is possibly due to the abnormally large temperature coefficient of the liquid at this point. The dielectric constant is 5.94 at  $25^\circ$  and 8.16 at  $0^\circ$ , so the error in the value 1.0243 could be caused by about  $0.1^\circ$  difference in the temperature of the cell when measured on the two systems.

The relation between these two measuring systems  $S_1$  and  $S_2$  having been obtained, the air capacity of each dielectric container can now be evaluated in terms of  $S_2$  by multiplying the value as determined on  $S_1$  by the conversion factor. For instance, the air capacity of condenser I in terms of  $S_1$  is  $8.311 \pm 0.005$ , and since the conversion factor is  $1.0276 \pm 0.0003$ , the value on the scale of  $S_2$  will be  $8.531 \pm 0.008$ . As measured directly on the scale of  $S_2$ , however, it is found to be  $8.54 \pm 0.03$ , and hence the increase in accuracy that has been obtained is obvious.

In conclusion, it must be observed that with an air capacity of  $8^\circ$ , the standard condenser will only cover the range of dielectric constant up to about 20, and therefore the scale was extended by means of auxiliary fixed condensers in just the same manner as was done for the system  $S_1$ . In this case, however, two Sullivan mica condensers were used of the same type as those described previously and of nominal value 0.001 and 0.002 microfarad respectively, and this extended scale was capable of dealing with dielectric constants up to 60. The method of connexion of these auxiliary condensers was the same as that noted previously, the screen terminal of each being kept permanently in circuit, and connexion being made as required by means of small mercury cups connected to the other terminals.

#### *The Experimental Condenser.*

The satisfactory design of the dielectric container is difficult, and probably most of the discrepancies occurring in the literature are to be attributed to errors in this respect. The essential features of an ideal condenser may be summarised thus (compare Hartshorn, *loc. cit.*) :

1. Its volume capacity should be reasonably small, since many of the organic liquids requiring investigation are expensive and difficult to prepare in bulk.
2. The electrostatic capacity should be as large as possible in order to secure the maximum accuracy of which the measuring system is capable.
3. It must be mechanically rigid, so that it may be handled without fear of any displacement of the conducting system and consequent alteration in capacity.
4. It must be easily cleaned and dried.



5. It must permit of accurate temperature control, and (of somewhat less importance) should be of such shape that it acquires the temperature of the thermostat fairly rapidly.

6. In this work, one other condition has been added that is not always required, *viz.*, that the condenser should be an absolute one, *i.e.*, it should afford direct proportionality between dielectric constant and measured capacity. This point needs explanation. Imagine the ideal case of two conductors placed in a vacuum at an infinite distance from all other conductors. If their capacity could be determined and then the whole of the surrounding space filled with some medium of dielectric constant  $\epsilon$ , the capacity would be increased accurately in the ratio  $\epsilon : 1$ . The same would hold good of two conductors within a closed conducting shield: the measured capacity would be  $C_{12} + C_1 C_2 / (C_1 + C_2)$ , where  $C_{12}$  is the inter-capacity between the conductors, and  $C_1$  and  $C_2$  are the capacities between each conductor and the shield separately, and then, provided the whole of the space within the shield were filled with the medium concerned, not only  $C_{12}$  but also  $C_1$  and  $C_2$ —and hence the effective measured capacity—would be proportional to the dielectric constant. If, however, the medium does not fill the whole space, this exact proportionality will no longer hold.

In practice this ideal case cannot be realised owing, first, to the leads which have to pass outside the shield to the measuring system, and secondly, to the need of some mechanical support which will fix the two conductors in a rigid position relative to each other and to the screen. It is possible, however, to overcome the difficulty of the leads by arranging that they make and break contact at the surface of the conductor by means of a very small movement, so that if they are of thin wire and pass through correspondingly small apertures in the shield, the change in their own capacity when contact is made becomes vanishingly small compared with the capacity being measured. It is quite a different matter with the second defect. Obviously no system can be devised which shall have no solid dielectric at any part of the field of force, although it is possible to dispose the solid in such a way that it only influences the shield capacities and does not intercept any of the lines of force between the two conductors. If in such a case measurements are made so that  $C_{12}$ ,  $C_1$ , and  $C_2$  can all be found individually (Giebe and Zickner, *Arch. Elekt.*, 1922, 11, 109; Hartshorn, *Proc. Physical Soc.*, 1924, 36, 399) and the lead correction is eliminated as above, the values of  $C_{12}$  thus found will be directly and accurately proportional to the dielectric constant of the medium, just as in the preceding hypothetical cases. It is at this point, however, that one great merit of the bridge method becomes apparent, *viz.*, that by means

of the Wagner or Monasch earth device, these shield capacities can be eliminated, so that one measurement is sufficient to determine  $C_{12}$ , as opposed to the three which are required by the other method. This represents not only a certain increase in accuracy, but a considerable saving in time, even in the case of the dual setting necessitated by the Wagner arm.

An alternative way of obtaining direct proportionality between measured capacity and dielectric constant is to determine a virtual capacity. This was the method adopted by Nernst for his absolute dielectric-constant determinations (*Z. physikal. Chem.*, 1894, 14, 634).

The virtual condenser method is not, however, well suited for routine determinations since, not only has the condenser to be filled and emptied a number of times for each determination, but also the use of four capacity readings instead of two to calculate the dielectric constant increases the probable error. On the other hand, the design of an absolute condenser has usually been achieved only at the expense of using a large volume of liquid. The majority of workers have therefore favoured some kind of relative condenser which can be calibrated in terms of liquids of known dielectric constants.

Consider the system discussed previously of two conductors within a closed conducting shield, and let us suppose this time that some part of the space is filled with a solid dielectric. Then, in general, any elementary tube of force from one conductor to the other will pass partly through a vacuum and partly through the solid, and the total element of capacity between the conductors due to this tube will be the series addition product of these portions. That is, if  $\Delta C_v$  and  $\Delta C_s$  represent the capacities due to vacuum elements and solid elements, respectively, the total contribution made to the capacity of the system by this tube of force will be  $1 / \left( \frac{1}{\Delta C_v} + \frac{1}{\Delta C_s} \right)$ . Let this be written as  $1 / \left( \frac{1}{c_v} + \frac{1}{c_s} \right)$ . The total capacity between the conductors will then be  $c_1 = \Sigma 1 / \left( \frac{1}{c_v} + \frac{1}{c_s} \right)$ , the summation being performed over all the tubes of force. If now a liquid of dielectric constant  $\epsilon$  is introduced, it may be assumed as a first approximation that the shape of the field of force remains unaltered, and the new capacity will be  $C_1 = \Sigma 1 / \left( \frac{1}{\epsilon c_v} + \frac{1}{c_s} \right)$ . The validity of this assumption will be examined later.

For the purposes of measurement it is necessary to express  $\epsilon$  as a function of  $c_1$  and  $C_1$ , but it is evident that in this general case there is no deducible relationship. There are two cases, however,

in which a simplification is practicable. (1) If the term due to  $c_s$  vanishes throughout the summation we have  $C_1 = 1/\Sigma \frac{1}{\epsilon c_v}$  or  $C_1 = \epsilon \times \text{constant}$ , corresponding to the case of an absolute condenser already discussed. (2) If either  $c_v$  or  $c_s$  vanishes for each individual term of the summation,

$$C_1 = \Sigma 1 / \left( \frac{1}{\epsilon c_v} \right) + \Sigma 1 / \left( \frac{1}{c_s} \right) \\ = \epsilon \Sigma c_v + \Sigma c_s$$

thus affording a simple linear relation between  $\epsilon$  and  $C_1$ . This evidently means that such a linear relationship holds if, and only if, each tube of force passes through only one medium. If the lines of force pass at any point from the solid to the liquid, it will not be possible to write  $C_1 = A\epsilon + B$ , where  $A$  and  $B$  are constants depending only on the geometrical configuration of the system and the dielectric constant of the solid medium. The importance of this limitation was definitely recognised by Nernst (*Z. physikal. Chem.*, 1894, 14, 633), although subsequent workers have sometimes ignored it.

The majority of routine measurements by previous investigators have been made with condensers for which the capacity has been assumed to be a linear function of the dielectric constant, i.e.,  $C = \epsilon c_v + c_s$ , the calibration constants  $c_v$  and  $c_s$  being determined from the air capacity and the capacity when filled with some liquid of known dielectric constant. This method suffers from certain drawbacks in our present state of knowledge. First, in view of the limitations under which strict proportionality between measured capacity and dielectric constant has been shown to exist, it does not appear very satisfactory to use only one liquid for calibration purposes over the whole range. Theoretically, the calibration should be performed with a number of liquids such that the range of dielectric constant to be investigated is covered fairly uniformly, and if then it is found that the capacity values so determined are linearly related to the corresponding known dielectric constants it will be permissible to equate the dielectric constant of any other liquid to  $(C - c_s)/c_v$ . Otherwise, an attempt may be made to represent the results by some empirical expression containing more than two constants, or the capacity may be plotted against the dielectric constant and the value for any unknown liquid read off from the graph. But here the second drawback to this relative condenser method makes itself felt. Not only are there too few liquids of accurately known dielectric constant to show whether strict linear relationship does hold or not, but it is evident that,

even if it does, the accuracy of the results obtained can never exceed that assumed for the calibrating liquids.

It was pointed out by Hartshorn (*loc. cit.*) in his work on benzene that the obvious criteria to be satisfied by such calibrating liquids are stability, ease and certainty of purification, reasonable cheapness, and (most important) fairly low conductivity, and the number of liquids satisfying these conditions is extremely limited. There are a few from about 2 to 2.5, of which benzene is undoubtedly the best; over the higher ranges, however, apart from chloroform (5), pyridine (12), and nitrobenzene (35), the author has failed to find any which have not some serious drawback to their use as calibrating standards.

Table II gives the results (corrected to 0°, 25°, and 50°) obtained by some of the previous workers for benzene, chloroform, and nitrobenzene.

TABLE II.

*Benzene.*

	25°.	50°.		25°.	50°.
Nernst .....	2.22		Graffunder .....	2.268	2.219
Drude .....	2.25		Grützmacher .....	2.277	2.224
Turner .....	2.274		Meyer .....	2.234	2.197
Tangl .....	2.274	2.223	Sayce and Briscoe ...	2.240	
Errera .....	2.26		Harris .....	2.248	
Isnardi .....	2.268	2.221	Hartshorn .....	2.273	2.223

*Chloroform.*

	0°.	25°.	50°.
Nernst .....		5.08	
Drude .....		4.80	
Turner .....		5.05	
Tangl .....		4.77	4.37
Isnardi .....	5.25	4.77	4.37
Grützmacher ...		4.95	4.59
Meyer .....	5.14	4.63	4.24
Harris .....		4.64	

*Nitrobenzene.*

	25°.	50°.
Turner .....	35.0	
Errera .....	32.6	
Jezewski .....	34.3	30.0
Meyer .....	32.3	28.4
Lange .....	36.5	
Harris .....	34.1	

*References.*—Nernst, *Z. physikal. Chem.*, 1894, **14**, 622; Drude, *ibid.*, 1897, **23**, 269; Turner, *ibid.*, 1900, **35**, 385; Tangl, *Ann. Physik*, 1903, **10**, 748; Errera, *J. Physique*, 1922, **3**, 401; Jezewski, *ibid.*, p. 293; Isnardi, *Z. Physik*, 1922, **9**, 153; Graffunder, *Ann. Physik*, 1923, **70**, 225; Grützmacher, *Z. Physik*, 1924, **28**, 342; Meyer, *Ann. Physik*, 1924, **75**, 801; Sayce and Briscoe, *J.*, 1925, **127**, 315; Lange, *Z. Physik*, 1925, **33**, 169; Harris, *J.*, 1925, **127**, 1049; Hartshorn, *Proc. Roy. Soc.*, 1929, **A**, **123**, 664.

In view of these discordant results it was obviously necessary to use some type of absolute condenser for the present work, and it was found that they fall into two main classes: (1) the virtual capacity type referred to previously; (2) condensers in which some attempt has been made to ensure that the whole of the lines of force giving rise to the measured capacity pass through the homogeneous medium. In general it is by no means apparent that

the condensers used by such workers as Grützmacher, Graffunder, Isnardi, or Jezewski were strictly absolute, and although in the absence of detailed dimensions it is difficult to discuss the probable magnitude of the deviation, the author is of the opinion that the greater part of the above discrepancies are to be attributed to this cause, together with the closely allied error introduced by the leads.

For reasons already stated, it was decided to exclude virtual capacity condensers from the scheme of the present work. Some time was spent initially with parallel-plate condensers, but satisfactory results were not obtained. Eventually it was decided to adopt the design first introduced by Sayce and Briscoe (*loc. cit.*) as a basis for further work. Three modifications were constructed, of which the first was uncorrected for the end effect, and the second and third had two completely different devices for eliminating this error.

*Condensers.*—*Condenser I* (Fig. 3). This consisted essentially of two concentric glass tubes sealed one within the other, the inner surface of the outer and the outer surface of the inner being silvered over the straight portion of each so that the annular space between them served as the dielectric container. The outer tube was 22 mm. in diameter and the air gap was about 1 mm. Contact with the silver film was made by platinum wires sealed through the walls into side tubes A and B; it should be noted that for good contact these wires must be sealed on to the walls again at some other point besides that at which they pass through into the side tube. Silvering was performed as follows. The lower internal seal was first coated with paraffin wax by drawing up through the tube C a mixture of equal parts of wax and xylene at about 60°. After a few moments, the hot liquid was allowed to drain away leaving a film which, when cold, successfully resists the attack of the silvering solution. The latter was introduced in the same manner, at least three layers were deposited, and the condenser was washed by drawing through it a rapid current of distilled water. It was then dried, and the paraffin wax removed with warm xylene, the tube E being subsequently sealed off.

This cell has the advantage that the water of the thermostat can circulate through the inner cylinder *via* openings C and D, and extremely rapid and efficient temperature control can therefore be maintained.

*Lead capacities and method of shielding.* In normal use the condenser is sunk in a thermostat so that the water level comes to within about 2 cm. of the taps. Imagine that it is immersed in a silvering bath to this level so that a metallic film is deposited, not only round the body of the cell, but also round the glass tubes down

which the leads pass to the mercury contacts. In these circumstances the following capacities will come into play: (1) the capacity between the two silver films on each side of the annular space; (2) the capacity between each film and the shielding film through the glass wall; (3) the capacity of each platinum mercury contact with the shield; (4) the capacity of each copper lead with the shielding film around the glass side tubes; (5) the capacity between the leads over the length from the shielded tubes to the point at which they are connected to the bridge system. If now the screen is earthed and the bridge balanced by means of the Wagner earth point in the usual manner, capacities 2, 3, and 4 will not be measured, and the only capacity in circuit will be  $C_1 + C_5$ . Suppose now the leads to be raised in the side tubes so that they just do not make contact with the mercury. The capacity in circuit will then be  $C_5' + 1 \left( \frac{1}{C_a} + \frac{1}{C_b} + \frac{1}{C_1} \right)$ , where  $C_a$  and  $C_b$  respectively are the small capacities between the leads and the mercury contacts.  $C_1$  is large compared with  $C_a$  or  $C_b$ , and to a first approximation these may be assumed equal, so that the capacity in circuit may be written  $C_5' + C_a/2$ . Now this capacity  $C_a$  across the broken contact will fall off fairly rapidly as the degree of separation increases, and by making actual measurements on the capacity between a similar lead and the surface of mercury in a small U-tube, it was shown that with a 1-cm. gap the capacity could not be detected. Further the change from  $C_5$  to  $C_5'$  due to this 1 cm. increase in the length of the lead between the cell and the bridge is also much less than can be detected—the leads being about 10 cm. apart.

The change that occurs on separating the leads from the mercury contacts by about 1 cm. affords therefore an accurate measure of the capacity.

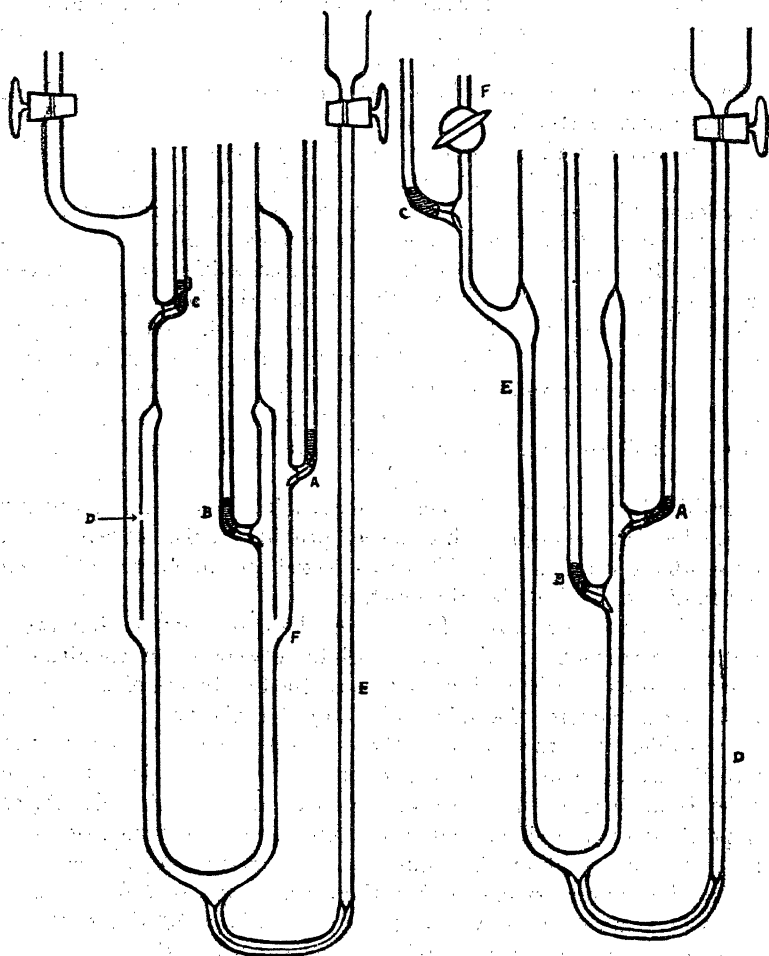
This result has been arrived at by assuming a metallic shield around the outside of the dielectric cell. It is found in practice, however, that identical results are obtained whether an earthed screen is provided, or whether the cell is merely placed in the water of the thermostat, and the latter earthed. Tap water has a sufficiently high conductivity from this point of view for it to be regarded as a conductor and not as an insulator.

*The end effect.* It is true that in this cell there is no solid dielectric at any point between the two films which constitute the plates of the condenser (referred to subsequently as the condenser films), but there is sufficient uncertainty regarding the distribution of the field at the extremities to prevent its being regarded *a priori* as a satisfactory form of absolute condenser; it appears possible that

some of the lines of force may bend round so that they pass not only through the dielectric medium but also through the glass walls, although in view of the earthed shield on the other side of each wall, this error is not likely to be large. Condensers II and III

FIG. 4.

FIG. 5.



were therefore constructed with a view to eliminating this possibility entirely.

*Condenser II* (Fig. 4). In this cell the two glass cylinders corresponding to those in condenser I were sealed together at the top only, the outer being drawn off at the bottom to a fairly wide-bore capillary. About 8 cm. below the seal, another intermediate cylinder

was joined as shown, and this had a small hole indicated at D. The annular space below the point F at which this cylinder terminates was about 10 cm. long with an air gap of 1 mm. Silvering solution was poured into the side tube E until it filled the whole cell to the level of the platinum contact C, a large air bubble, however, being trapped between the inner cylinder and the intermediate one above the hole in the latter. The inside of the inner cylinder was also silvered up to the level of the contact C. The contacts A and B were connected to the bridge in the usual manner, and C was kept permanently earthed.

It is evident that the capacity being measured between the contacts A and B is constituted solely by the field between the condenser films below F, *i.e.*, the end effect in condenser I has here become divided in two between the earthed film and each condenser film respectively, and these earth capacities are, of course, not measured. In other words, the whole of the lines of force giving rise to the capacity between A and B pass through the lower annular space only. This contains an absolutely homogeneous medium and the only points at which distortion of the field can occur due to the dielectric constant of the medium are the extremities of the two condenser films—and these are too remote for there to be any effect on the field at F.

If this view is correct, the measured capacity should be independent of the level of the liquid filling the cell provided it rises at least 1 cm. or so above the point F. This was tested and found to hold even for liquids of high dielectric constant.

*Condenser III* (Fig. 5). In this cell the end effect is eliminated, not by an earthed cylinder intermediate between the extremities of the two condenser films, but by two earthed cylinders placed above and concentric with them, in such a way that the air gap is as small as possible. In other respects the construction was similar to the two preceding cells. Silvering solution was poured into the side tube D until it rose in the annular space to the point E. After deposition of the silver had been completed, the condenser was inverted and another film was deposited from the side tube F up to the annular space so that there was only about 1 mm. gap between it and the previous film. A and B were the contacts connected to the bridge and C was earthed. For measuring purposes, the level of the liquid in the side tube was adjusted until it had risen at least 1 cm. above the point E.

Two other errors may arise through faulty condenser design, *viz.*, (a) the series resistance error discussed on p. 572, and (b) polarisation capacities.

(a) For the investigation of the first, condenser I was silvered



without a preliminary treatment with paraffin wax, so that the silver film was continuous between the contacts A and B, and the resistance between these points was then measured and found to be about 7 ohms for one deposit of silver, 4 ohms for two, and 2 ohms for three. It was evident that the terminal or contact resistance was small, and that the effective series resistance was that due to the internal resistance of the films.

Measurements were also made on condensers II and III, by pouring in a quantity of saturated potassium chloride solution so that the condenser films were short-circuited at the bottom; in each case the resistance (for three layer deposits) was about 2 ohms.

Now, of the liquids for which accurate results are quoted subsequently, nitrobenzene had the highest conductivity, and the equivalent shunt resistance of the condensers was therefore a minimum when filled with this at 80°, the actual value being about 5000 ohms. Hence (see p. 572), the error caused by a 2-ohm series resistance was less than 0.1%, and at lower temperatures and for other liquids it was, of course, still smaller.

(b) The possibility of an error due to polarisation capacities was investigated in the case of the liquids of higher conductivity by varying the intensity of the oscillator output, and hence the current density through the cell, over at least a five-fold range. No change in the measured capacity was detected.

#### *Apparatus and Procedure.*

*The Generator.*—The triode valve oscillator has now completely supplanted the older types of generator, not only by reason of its ease of manipulation, but by virtue of the purity of wave form obtainable. The actual instrument used was made by Cambridge & Paul. It had a variable capacity unit, by means of which the frequency could be varied between 100 and 5000, and also 3 secondary windings which permitted of the output intensity being varied within fairly wide limits. Satisfactory results were obtained either with an R valve, or a dull emitter valve, or (if more power was required) with a valve of the LS5 type. In general, however, with liquids of any appreciable conductivity, it was found much better to reduce the intensity as far as possible in order to minimise heating effects in the bridge.

*The Detector.*—A 1000-ohm Brown telephone was used, but since it was found that a low output from the oscillator did not give sufficient sensitivity, a two-valve amplifying circuit was introduced between the bridge and the telephone. The components used were two D.E.L. 410 valves and a Marconi Ideal Transformer of ratio 4:1; this amply intensified the effect, but the quality of the note

suffered considerably from the introduction of harmonics. These, however, were almost entirely eliminated by shunting the telephone with a condenser of suitable value to by-pass the notes of higher frequency. Too large a capacity will begin to reduce the intensity of the fundamental, and an optimum value was sought at which the selective reduction of the overtones was a maximum. For a fundamental note of 1000 frequency, a 0.15 microfarad capacity gave satisfactory working.

*Bridge Components.*—The ratio arms were two Sullivan 1000-ohm non-reactive coils guaranteed equal to each other to within 0.01%. The standard condenser (see p. 577) was fitted with a wooden arm so that it could be controlled from a distance of 8 or 9 feet. The capacity in the second arm of the bridge required to balance that in the measuring arm was made up by a 0.001 microfarad Dubilier variable air condenser, together with two fixed mica condensers of 0.001 and 0.002 microfarad capacity respectively. The compensating resistances were as previously described (p. 575).

*The Wagner Earth-point System.*—This system (referred to subsequently as the Wagner arms) was constructed in the case of liquids of low conductivity to imitate the main bridge system, *i.e.*, one arm consisted of a 1000-ohm fixed resistance, and the other of a variable capacity shunted by a variable liquid resistance. In the case of liquids of higher conductivity, it was found preferable to make the total impedance of the Wagner arms large compared with that of the bridge, and hence a fixed 0.01 microfarad condenser was used in one arm, while a variable wire resistance (max. 10,000 ohms) in series with a variable condenser (max. 1 microfarad) constituted the second. It is, of course, not necessary that the Wagner arm components should be of the same degree of perfection as those used in the main bridge system.

*Bridge Set-up.*—The oscillator was placed about 8 feet from the nearest bridge component and was surrounded by an earthed screen, while the amplifier was similarly screened and placed about 6 feet away on the further side of the bridge, the observer being situated just beyond. Connexion between the oscillator, bridge, and amplifier was made by means of armoured flex, the sheath being earthed. All the bridge component shields were connected to one or other of the oscillator points, and were mounted on blocks of paraffin wax.

It was found that the bridge was reasonably free from external influences—in particular the balance point was independent of the observer's position provided he did not approach to within less than 2 feet, and the capacity balance could often be accurately reproduced over a period of hours. Direct action from the oscillator

was negligible, reversal of the connexions to either the bridge or telephone terminals causing no change in the balance point.

*Temperature Control.*—A gas-heated thermostat was used for temperatures above  $18^{\circ}$ , and maintained constant to within  $\pm 0.02^{\circ}$ . Temperatures below  $18^{\circ}$  were suitably controlled by using a bath of large volume insulated with felt, and by working at a temperature within a few degrees of that of the room, the latter also being maintained as constant as possible. Under these conditions, the thermometer reading could be kept within  $0.05^{\circ}$  over at least  $\frac{1}{2}$  hour. The bath at  $0^{\circ}$  was maintained with tap water and ice (p. 586), the exact temperature being observed on a thermometer. In a number of cases the results quoted have been reduced to even temperatures by using the appropriate temperature coefficient, but such corrections were not used for differences of more than  $\frac{1}{2}^{\circ}$ . The thermometer was calibrated against another standardised at the N.P.L.

*Method of Measurement.*—The following scheme was adopted systematically for all the measurements recorded. The bridge and Wagner arms were first set to approximate balance with the condenser to be determined in circuit, and since, with practice, this could be done fairly accurately, the need for a large number of successive adjustments was avoided. The current was then switched on, each balance corrected to a minimum, and then an accurate bridge balance made from a distance. The standard condenser was set at least twice (once from each direction), and it was usually found (except in the case of liquids of high conductivity) that these readings agreed as closely as could be observed on the vernier. The experimental condenser was removed from circuit, the bridge rebalanced as before, only the measuring system and compensating resistances in the same arm being altered, and finally the condenser was re-connected and the original balance checked to make sure that no shift in the bridge reading had occurred.

It should be noted that a definite displacement of the Wagner arms by an amount considerably greater than the sensitivity of their balance makes no perceptible difference to the bridge reading.

### Results.

(1) *Intercomparison of the Dielectric Containers.*—Table III gives the dielectric constants of a number of liquids as determined at  $25^{\circ}$  in the three cells described previously. The values are quoted only for the purpose of showing the relationship between these condensers, and are not necessarily (except in the case of benzene) to be taken as accurate data for the liquids in question, since no special purification was undertaken beyond that necessary to obtain a reasonably low conductivity, i.e., less than  $10^{-7}$ . The

reproducibility of the results was checked throughout by making two distinct sets of observations on each condenser after emptying and refilling it. As an example, the capacities on the second measuring system for the mixture of toluene and amyl alcohol in condenser III were :

1st Series .....	86.61	86.60	86.63	} Mean 86.61
2nd Series .....	86.61	86.62	86.58	

The air capacities of all three condensers on  $S_1$  were :

Condenser.	Number of observations.	Range of observations.	Mean.
I	15	8.299—8.323	8.310
II	16	5.952—5.969	5.956
III	14	7.920—7.945	7.933

Hence the dielectric constant for this mixture relative to air was  $86.61/7.933 \times 1.0276 = 10.626$ .

TABLE III.

	Air = 1.			Benzene = 1.		
	I.	II.	III.	I.	II.	III.
Hexane .....	1.910	1.911	1.914	0.8414	0.8409	0.8414
Benzene .....	2.270	2.273	2.275	—	—	—
Acetal .....	3.790	3.795	3.800	1.670	1.670	1.670
Chloroform .....	4.717	4.723	4.728	2.078	2.078	2.078
Dimethylethylcarbinol	5.929	5.936	5.946	2.612	2.612	2.613
Toluene-amyl alcohol mixture	10.577	10.615	10.626	4.654	4.670	4.670
isoButyl alcohol .....	17.88	17.95	17.98	7.874	7.901	7.905
o-Nitrotoluene .....	26.54	26.69	—	11.69	11.74	—
Nitrobenzene .....	34.76	34.88	34.92	15.32	15.35	15.35

The dielectric constants relative to air (Table III) show that condensers II and III are in fair agreement, the latter affording results consistently high by about 0.1—0.15%, and that the results given by condenser I are distinctly low—by about 0.5% over the upper range.

For the dielectric constants relative to benzene, the agreement between condensers II and III is extremely good, and hence it appeared probable that the discrepancy between them on the air basis might be due to an error in the air capacity determination of one of them. The benzene measurements were therefore repeated with two samples of specially purified material, and the results obtained were :

Sample.	Condenser.	Capacity.	$\epsilon$ .
A	II	13.536	2.273
B	II	13.534	2.273
A	III	18.048	2.275
B	III	18.043	2.275

These values were then taken as standard, and the dielectric constant of benzene at  $25^\circ$  assumed to be 2.273 (Hartshorn, *Proc. Roy.*

*Soc.*, 1929, A, **123**, 664); the air capacities calculated on this basis were 5.955 and 7.939.

The agreement between observed and calculated values is exact in the case of condenser II, and for condenser III the difference is less than 0.1%, the calculated value falling well within the range of observations. This discrepancy is too small to justify any conclusions being drawn, and the values calculated from the benzene capacities are therefore taken as standard; on this basis, both condensers II and III afford direct proportionality (within 0.1%) between dielectric constant and measured capacity.

Thus, these two condensers, which have different devices for eliminating the end effect, afford concordant results over the whole scale investigated, within the limits of experimental error. Condenser I, however, which is uncorrected for the end effect, does not agree with them over the whole range either with air or with benzene as unity. Further comment on the discrepancies shown by Condenser I is postponed, but it is claimed that both Condensers II and III are free from errors due to the end effect.

It was also necessary to consider the temperature variation of these condensers. It may be assumed that the silver film expands at the same rate as the glass, and if the coefficient of expansion of glass is taken as  $10^{-5}$ , a change of  $100^{\circ}$  will only produce 0.1% change in the dimensions of the cell. Further, such change as does occur will increase the area of the plates and also the distance between them, and these two effects will tend to neutralise each other with regard to capacity changes. It is to be expected, therefore, that the change in capacity over  $100^{\circ}$  range should be too small to be detected, and this is borne out by the following results.

In the first place the air capacities of condensers I and II were measured at  $0^{\circ}$ ,  $25^{\circ}$ , and  $80^{\circ}$ , the mean values being:

	$0^{\circ}$ .	$25^{\circ}$ .	$80^{\circ}$ .
Condenser I .....	8.309	8.311	8.308
Condenser II .....	5.952	5.956	5.957

Secondly, the benzene capacities for the first condenser were measured at  $25^{\circ}$  and  $50^{\circ}$ , and the air capacities calculated on this basis, assuming the dielectric constant of benzene to be 2.273 at  $25^{\circ}$  and 2.223 at  $50^{\circ}$  (Hartshorn, *loc. cit.*), are 8.303 and 8.302 respectively.

It is concluded, therefore, that this type of dielectric container has no appreciable temperature coefficient of capacity, and for the purpose of the next section the air capacities have been assumed to be

	II.	III.
Measuring system $S_1$ .....	5.955	7.939
" " $S_2$ .....	6.119	8.158

*Purification of benzene.* The first of the samples referred to above had been purified by Harris (J., 1925, 127, 1063) for dielectric-constant determinations. It had been standing over sodium wire in the meanwhile, and was distilled once before use. The second sample was purified by the author from A.R. benzene by Richards and Shipley's method (J. Amer. Chem. Soc., 1914, 36, 1825).

(2) *The Dielectric Constants of Certain Purified Liquids at 0—80°.*—(a) *Standard liquids at 25°.* *Benzene.* The results obtained for two samples of specially purified benzene have been summarised on p. 592. They were subject to a probable error of about 0.1% on the air-capacity determination, and of 0.05% on the benzene, thus affording a mean value of  $2.274 \pm 0.004$ : the figure  $2.2725 \pm 0.0005$  which has been accepted from Hartshorn's work (*loc. cit.*) lies well within these limits.

*Chloroform.* Three samples of different origin (one from B.D.H. and two from Hopkin and Williams) were purified by the same method. Each was shaken for 15 minutes with concentrated sulphuric acid, washed twice with dilute sodium hydroxide solution and five times with water, dried over ignited potassium carbonate, and fractionated until a main fraction was obtained boiling within less than 0.1°. This was kept over calcium chloride in a dark cupboard, and immediately before use was decanted, shaken for a few minutes with a little solid sodium hydroxide, and distilled.

The results obtained are given in Table IV. The probable error in the air capacity as adjusted by the benzene values is certainly less than 0.1%, and in the chloroform capacities 0.02%, the total error therefore being 1 part in 800 parts; the mean value accepted for chloroform at 25° is  $4.724 \pm 0.006$ .

*Nitrobenzene.* Sample A. This had been purified by Harris, and distilled completely at practically constant temperature. It was therefore merely dried over calcium chloride and distilled twice in a vacuum, having then a conductivity of the order  $10^{-7}$  mho. (In the author's experience, the easiest way to obtain good conductivities is to use as high a vacuum as possible for the final distillations: throughout this work 1 mm. or less has been employed for all liquids of high boiling point.)

Sample B. This was B.D.H. material. It was fractionated four times in a vacuum, only one-third of the original bulk being retained. It was then dried over calcium chloride and distilled twice in a vacuum;  $\kappa = ca. 10^{-7}$ .

Sample C. This was synthesised from some of the benzene purified as above, care being taken to prevent the temperature rising above 50° during nitration; the nitrobenzene layer was separated, shaken once with water and four times with sodium

carbonate solution, steam-distilled in the presence of sodium carbonate, dried over calcium chloride, and then twice distilled in a vacuum;  $\kappa = \text{ca. } 0.5 \times 10^{-7}$ .

The results obtained are given in Table V. The probable error in the nitrobenzene capacity determinations can safely be taken as 0.05%, but in this case, as opposed to that of chloroform, there is an additional error of 1 part in 3000 parts due to the conversion factor between the two measuring systems (p. 580). The total probable error will therefore be less than 1 part in 600 parts, and the mean value accepted for nitrobenzene at 25° is  $34.89 \pm 0.05$ . Although two samples were dried over phosphoric oxide for one week and six weeks respectively, no change in the dielectric constant was noticed (see Table V).

*Benzonitrile.* The material used was kindly provided by Dr. Martin, and had been purified in the same manner as that used for his conductivity work (*loc. cit.*). The results obtained for two different samples are given in Table VIII. These values showed no variation with frequency or current intensity, and the probable error is the same as for the nitrobenzene determinations.

(b) *Temperature variations.* Determinations of the dielectric constant of chloroform at temperatures between 0° and 50° were made in condensers II and III with each of the three specimens described, and the mean of the six results at each temperature is given in Table VI. Similar determinations were made for nitrobenzene at temperatures between 10° and 80° (Table VII).

In each case, when these results were plotted against temperature on a very open scale, they lay on a smooth curve within the limits of experimental error quoted.

(c) *Frequency variations.* Determinations of the dielectric constants of both chloroform and nitrobenzene at 25° and 50° were made at frequencies between 500 and 2500, but in no case was any change detected.

TABLE IV.  
*Chloroform at 25°.*

Sample.	Condenser.	Measuring system.	Capacity.	$\epsilon$ .
A	III	S <sub>1</sub>	37.500	4.723
A	II	S <sub>1</sub>	28.132	4.724
B	II	S <sub>1</sub>	28.125	4.723
C	II	S <sub>1</sub>	28.126	4.723
C	III	S <sub>1</sub>	37.502	4.724
B	II	S <sub>2</sub>	28.90	4.723
B	III	S <sub>2</sub>	38.66	4.726
C	II	S <sub>2</sub>	28.92	4.726
				Mean 4.724

TABLE V.

*Nitrobenzene at 25° (approx.).*

Sample.	Drying agent.	Condenser.	Temp.	Capacity.	$\epsilon$ .	$\epsilon_{25^\circ}$ .
A	CaCl <sub>2</sub>	II	25.0°	213.55	34.90	34.90
A	"	III	25.0	284.6	34.89	34.89
A	"	II (repeat)	25.0	213.4	34.87	34.87
B	"	II	25.2	213.4	34.87	34.91
B	"	II	25.2	213.2	34.84	34.88
B	"	II	25.2	213.3	34.86	34.90
C	"	II	25.0	213.4	34.87	34.87
C	"	III	25.0	284.7	34.90	34.90
B	P <sub>2</sub> O <sub>5</sub>	II	25.0	213.65	34.91	34.91
B	"	II (repeat)	25.1	213.4	34.87	34.89
						Mean 34.89

TABLE VI.

*Chloroform.*

Temp. ....	0°	11.2°	18°	25°	30°	40°	50°
$\epsilon$ .....	5.189	4.971	4.848	4.724	4.636	4.473	4.310

TABLE VII.

*Nitrobenzene.*

Temp.	10°	12.8°	18°	25°	30°	32.9°	40°	54°	60°	80°
$\epsilon$ .....	37.85	37.30	36.23	34.89	33.97	33.48	32.26	29.99	29.08	26.28

TABLE VIII.

*Benzonitrile.*

Temp. ....	0°	18°	25°	40°	50.3°	60°	70°
$\epsilon$ (sample 1) .....	27.60	—	25.20	24.01	—	22.67	22.10
$\epsilon$ (sample 2) .....	27.58	25.85	25.21	24.02	23.28	—	—

In conclusion, the author desires to express his most sincere thanks to Professor J. C. Philip, F.R.S., for suggesting this subject for research, and for his constant interest and inspiration. He also wishes to acknowledge grants in assistance of this work from the Department of Scientific and Industrial Research and from the Portsmouth Higher Education Committee.

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# LXXXI.—*The Photolysis of Aqueous Hydrogen Peroxide Solutions. Part I. Experimental Methods.*

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THE decomposition of hydrogen peroxide solutions by light has been the subject of a number of previous investigations (Tian, *Compt. rend.*, 1910, 151, 1040; 1913, 156, 1601, 1758, 1879; *Ann.*



*Fac. Sci. Marseille*, 1915, **22**, 197; *Ann. Physique*, 1916, **5**, 248; Henri and Wurmser, *Compt. rend.*, 1913, **156**, 1012; **157**, 126, 284; *J. Physique*, 1913, **3**, 305; Matthews and Curtis, *J. Physical Chem.*, 1914, **18**, 166, 521; Kornfeld, *Z. wiss. Phot.*, 1921, **21**, 66; Anderson and Taylor, *J. Amer. Chem. Soc.*, 1923, **45**, 650, 1210; Rice and Kilpatrick, *J. Physical Chem.*, 1927, **31**, 1507), but in spite of this work, and although the reaction is, chemically, very simple, very little can be said about its mechanism, many points remain obscure, and there are some very curious contradictions. One of the more obvious may be mentioned: Henri and Wurmser published, in the same year, two papers (*loc. cit.*) dealing with the quantum efficiency of the reaction in the region 200–300  $\mu\mu$ ; in the one, using full light from a cadmium spark, they found  $\gamma$  to have an average value of 130; in the other, using the dispersed light from a zinc spark, they found  $\gamma$  over practically the same spectral region to vary between 4.4 and 5.8.

Our work has been essentially directed to an investigation of the relations between degree of decomposition and absorbed light over a wide range of concentration, far greater than any hitherto worked with. In the majority of the experiments, the active light has been monochromatic or confined to a fairly narrow spectral region. Except quite incidentally, we have not touched the subject of the effect of additions to the photolyte, whether inhibitors or accelerators.

#### EXPERIMENTAL.

*Hydrogen Peroxide.*—Three different varieties were employed. Some early experiments with dilute solutions were carried out on a specimen of perhydrol (Merck) intended for tropical export, and containing a nitrogenous thermal inhibitor. For much of the work, Merck's ordinary perhydrol (inhibitor-free) was used. When first insolated by 365  $\mu\mu$  light, this showed a strong bluish-green fluorescence, which decreased normally on dilution. Continued insolation completely destroyed this fluorescence, and its disappearance was accompanied by a marked decrease in the photosensitivity of the perhydrol, but by an equally marked increase in its rate of thermal decomposition. It is probable that the impurity causing the fluorescence was derived from the wax with which the perhydrol bottles are internally coated: this is yellow and has a distinct oily smell. It may be added that we found it very difficult to inhibit the photodecomposition of the concentrated perhydrol. Small additions of sulphuric acid to the cell contents were without effect, whilst 1 g. of concentrated acid only reduced the velocity by 30–40%.

The remainder of our experiments were carried out on hydrogen

peroxide prepared in the laboratory by the method of Kilpatrick, Reiff, and Rice (*J. Amer. Chem. Soc.*, 1926, 48, 3019), modified in certain respects. In the actual distillation of the first product, 200 c.c. were placed in the glass distilling flask, and the remainder added in 50-c.c. portions as the distillation proceeded. The flask had a volume of 500 c.c. and its neck was provided with two ground joints, one of which carried a thermometer suspended by platinum wire from the stopper, the other a tap-funnel for the addition of more solution. The outlet tube was bent upwards and terminated in a ground joint making connexion with the silica condenser, to which was attached, by another joint, the silica receiver. No lubricant other than condensate was employed on any of the joints, and practically no leakage resulted under the water-pump vacuum conditions (2 cm. of mercury) employed. The first 80% of the distillate consisted of a weak solution of hydrogen peroxide (0.1—0.3*M*) and was discarded. The final concentrated fraction was freed from traces of chloride by redistillation over small quantities of silver sulphate. The solutions thus prepared were 9—14*M*.

*Extinction Coefficients.*—These were determined for the chief lines of the quartz-mercury arc by the spectrometer-thermopile-galvanometer method, the transmissions of a small quartz cell filled with distilled water and with the peroxide solution being compared. For 365  $\mu\mu$  the cell was 4.62 cm. deep (internal) and several concentrations were measured. For 313 and 303  $\mu\mu$ , a 2.04-cm. cell was used, and one concentration only was investigated. For the shorter wave-lengths, the cell was 1.026 cm. deep and various concentrations were used. Table I contains the molecular extinction coefficients for redistilled Merck's perhydrol, calculated by the equation  $\log_{10} I_0/I = \alpha c d$ , where  $d$  is expressed in cm. and  $c$  in mols./litre. The measurements with the 365  $\mu\mu$  line were made by Mr. J. W. T. Spinks.

TABLE I.

$\lambda$ , $\mu\mu$ .	$c$ .	$\alpha$ .	$\lambda$ , $\mu\mu$ .	$c$ .	$\alpha$ .	$\lambda$ , $\mu\mu$ .	$c$ .	$\alpha$ .
365	11.63	0.00647	365	3.08	0.00655	280	0.0753	4.06
365	9.45	0.00669	313	0.459	0.39	265	0.0758	10.03
365	7.57	0.00663	303	0.459	0.86	265	0.0287	10.48
365	5.96	0.00668	297	0.238	1.31	265	0.01125	10.33
365	4.78	0.00683	289	0.238	2.16	254	0.0287	21.9
365	3.70	0.00673	280	0.238	3.73	254	0.01125	19.6

In one paper, Henri and Wurmser quote  $\alpha_{280} = 3.0$  and  $\alpha_{256} = 20$ . From the data in another of their papers can be calculated  $\alpha_{283} = 1.5$ ,  $\alpha_{275} = 4.9$ , and  $\alpha_{257} = 16$ . Kornfeld (*loc. cit.*) found 0.422 for 311  $\mu\mu$ . The agreement with these values is seen to be fairly good. On the other hand our figures are very different from those recently published by Urey, Dawsey, and Rice (*J. Amer.*

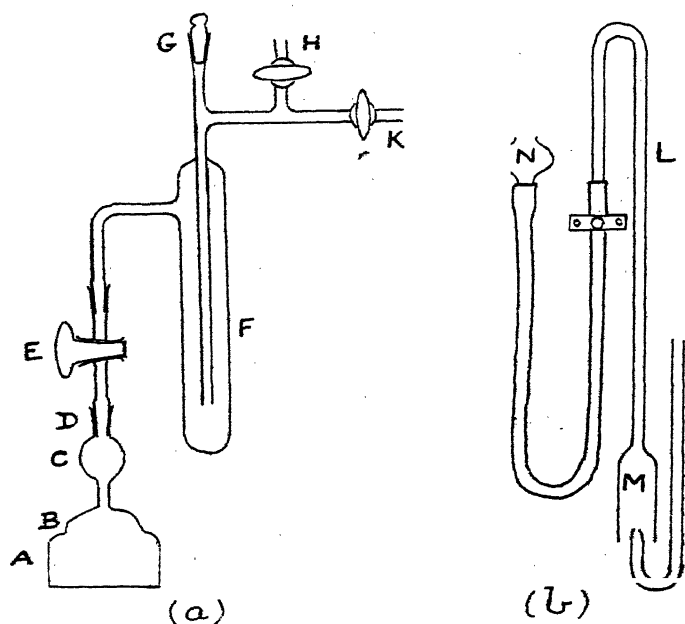
*Chem. Soc.*, 1929, 51, 1371), the two sets of  $\alpha$  values only approaching one another at the shortest wave-lengths measured by us; the discrepancies seem too great to be accounted for by the fact that our solutions were more concentrated.

*Reaction Cell.*—The type of apparatus employed was determined by the use, in the majority of our experiments, of such concentrated peroxide solutions as to make it impossible to follow the reaction with any accuracy by titration. The method used was to pump off, collect, and measure the oxygen formed, a procedure already adopted with success in this laboratory in the case of the photolyses of formic and of oxalic acid (J., 1926, 2834, 2854). The method offered the additional advantage of reducing to a minimum the possibility of contamination during the reaction by added inhibitors or accelerators. A Toepler pump of about 300 c.c. capacity was used for the evacuation of the reaction cell, the latter being provided with a tap and ground joints so that it could be opened for filling and cleaning and for attaching to the pump for evacuation before and after insolation. Early experiments showed the importance of keeping the photolyte away from contact with glass. Attempts to use a composite cell, built up of quartz plates and a glass block, the inner surface of the latter being coated with paraffin wax, failed, as the wax peeled off when the cell was evacuated. An attempt to construct a cell consisting of quartz plates fused on to a reinforced block of paraffin wax also failed, as the cell slowly caved in and developed leaks on evacuation. Finally, a fused silica cell was designed, with which, or its successor, the great majority of our results were obtained. This, with the adjacent parts of the Toepler pump, is shown in Fig. 1a.

ABCD is of clear fused quartz, the part A, through which the light beam passed, being 5 cm. long with circular plane parallel end-plates of 3 cm. diameter. B is a hemi-cylindrical dome, giving an adequate surface of liquid for evolution of oxygen, and ensuring that the level of the photolyte shall always be well above that of the beam of light. C is a bulb, serving to retain any peroxide carried up by "bumping" or by too violent an evolution of gas. Into the ground socket D fits the glass tap E, provided with another ground socket at its upper end, allowing of connexion with the evacuation apparatus. F is a trap in which, during evacuation, vaporised hydrogen peroxide and water vapour are condensed by immersion in an ether-solid carbon dioxide mixture. It is provided with a stopper G for removing this condensate when necessary. H is a tap for admittance of air, and connexion with the pump (300 c.c. barrel) is made through the tap K. Ramsay tap-grease was used for all taps and joints.

*Measurement of Evolved Gas.*—Fig. 1b shows the simple means employed for the measurement of the evolved gas. The inverted U-tube L was of about 3 mm. internal diameter (and thus of internal volume 0.070 c.c./cm.) and its longer limb was 40 cm. long. The extension M permitted of the introduction of the delivery tube of the Toepler pump. The shorter limb was connected by pressure tubing, controlled by a screw clip, with the mercury reservoir N. Prior to the collection of a sample of gas, the whole tube was filled with mercury and the screw clip closed. The gas was then pumped off and delivered into M, the diameter of L being sufficiently small

FIG. 1.



to prevent the gas rising further. On the completion of the evacuation, the latter was drawn into L by manipulation of N and of the screw clip, its temperature and pressure measured, and the length of the column read off by means of a scale placed immediately behind L.

*Manipulation.*—In view of the importance of the nature of the surface in all work with hydrogen peroxide, the treatment to which the reaction cell was subjected was as far as possible standardised. Before being filled, it was first cleaned with nitric acid containing a small quantity of alcohol, grease on the ground joint being thereby removed, and, after a thorough washing with distilled water, it

was rinsed out several times with a portion of the reaction solution, and filled nearly up to the dome. The ground joint D (Fig. 1a) was then lightly greased and put in position, being held down by rubber bands passing over the tap E and round the bottom of the reaction cell. E was very carefully greased and put together. It was of the utmost importance that this tap should function well, as it sometimes had to be turned several hundred times in the course of a series of experiments done on a single filling. The whole was then attached to the pump and evacuated as far as possible, E being opened at intervals. Continual attention (tapping and shaking of the cell) was necessary to avoid explosive bumping and gas evolution. The degree of evacuation feasible was limited by the thermal decomposition of the peroxide. With Merck's perhydrol, this was slow and caused no trouble. With the solution prepared by us, where the dark reaction for the cell contents might amount to perhaps 0.02 c.c. of oxygen per min., the method of evacuation had to be carefully standardised and its results watched in order to detect the stationary state at which the rate of removal of oxygen was just equalled by its rate of production.

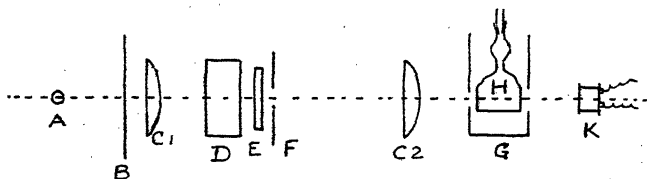
The moment of completion of the evacuation was noted and taken as the zero time of the dark reaction for which correction had subsequently to be made. With taps E and K closed, air was admitted by opening H, the cell detached, placed in the thermostat (see later), allowed to reach temperature equilibrium, and the insolation commenced. After the required interval (varying from a few minutes to a few hours) the cell was again attached to the pump, the tap H closed, and, after the evacuation of the air between E and K (sometimes carried out through H by a Hyvac pump in order to accelerate matters and reduce the "dark" correction), the gas in the cell was pumped off, collected, and measured as quickly as possible.

With perhydrol, the "dark" correction was usually only a few units %, and the duration of an insolation of the order of an hour. As already indicated, work with the solution prepared by us in the laboratory was far less easy. The quantum efficiencies were raised 10—20-fold, and the thermal reaction to an even greater extent. As the amount of decomposition permissible in a simple insolation was limited (a) by the desirability of avoiding any appreciable change in the concentration, and (b) by the possibility of too high a pressure loosening the joint D, it became necessary to reduce the time of insolation considerably, runs of 4 mins. not being uncommon. But clearly the time necessary for the evacuation and collection of the gas could not be reduced to anything like the same extent; even if the Hyvac pump was used whenever possible, 15—20 minutes

was about the shortest time required. Consequently, the thermal correction was considerable with this preparation—indeed, it was impossible to obtain results of value in the use of mercury light filtered by a chlorine filter (*q.v.*), where the intensities were comparatively low, for the thermal reaction considerably exceeded 50% of the total decomposition.

*Arrangement of Apparatus for Insolation Experiments.*—The general arrangement is shown in Fig. 2; A represents the source of light, B is a shutter, and  $C_1$  and  $C_2$  are crystal quartz lenses. D is a 5-cm. quartz water-cell, E the light filter, F a diaphragm with variable aperture (0.5—2.5 cm. diameter), and G a small thermostat containing the reaction cell H. Finally, K is the thermopile for the measurement of the incident and absorbed energy. All apparatus when necessary was firmly secured to an optical bench and, with the exception of the lamp and shutter, was covered by an internally blackened box,  $C_1$  being fitted into a hole cut in the side.

FIG. 2.



*Light Source.*—In every case this consisted of a K.B.B. quartz mercury lamp of the atmospheric pressure type; these had an advantage over the vacuum type for the present work because of their relatively high intensity, this being due to the short length of arc and to the fact that they can be overloaded and yet burn very steadily, provided that additional cooling be employed. We used 100—110-volt lamps, both of the horizontal and of the vertical pattern. Their normal rating is 2 amps. We burnt them at 3.5 amps. and 80 volts, a Tirrill regulator ensuring a steady supply voltage, and the lamps being cooled by an electric fan. The energy distribution of their radiation, a knowledge of which was necessary in consequence of the light filters not being monochromatic, was determined on several occasions during the work by a modification of standard methods already described (*J. Physical Chem.*, 1925, 29, 713). An example of the data obtained is given in Table II, *I* being the intensity relative to the 365  $\mu\mu$  line as unity.

*Light Filters.*—Four types of filter were used.

(a) Corning Glass Plate G.586 A.W. of 3.6 mm. thickness. Transmission — 0.77 of 365  $\mu\mu$  and 0.22 of 405  $\mu\mu$ ; 7% of the total radiation transmitted, when used in conjunction with the 5-cm.

TABLE II.

Horizontal arc, after 50 hours' running.

$\lambda$ , $\mu\mu$ .	<i>I</i> .	$\lambda$ , $\mu\mu$ .	<i>I</i> .	$\lambda$ , $\mu\mu$ .	<i>I</i> .	$\lambda$ , $\mu\mu$ .	<i>I</i> .
579	0.85	365	1.00	289	0.029	265	0.094
546	0.68	313	0.44	280	0.054	260—254	0.170
436	0.56	303	0.20	275	0.015	248	0.032
405	0.30	297	0.091	270	0.019	240—239	0.012

water filter, was red and infra-red. This correction was determined by means of a thermopile and a Zeiss red-glass filter which cuts off sharply below 600  $\mu\mu$  whilst transmitting about 85% of radiation between this limit and nearly 2  $\mu$ . The violet 405  $\mu\mu$  light is not appreciably absorbed by hydrogen peroxide.

(b) 1 Cm. of 0.1% aqueous potassium chromate solution between quartz plates. The transmission was

579	546	436	405	313	303	297 $\mu\mu$
0.80	0.88	0.71	0.63	0.44	0.39	0.30

10.3% of the total transmitted radiation was red and infra-red. The visible light is not absorbed by hydrogen peroxide.

(c) 5 Cm. of chlorine gas at 1 atm. pressure in a plane-parallel vessel of fused silica. The transmission was

579	546	436	405	280	265	256	248 $\mu\mu$
0.875	0.85	0.40	0.145	0.04	0.42	0.63	0.60

Used in combination with the mercury lamp, the average wavelength of the ultra-violet transmitted light was 256  $\mu\mu$ . For a few experiments, a similar 2-cm. filter was employed.

(d) A mixture of chlorine gas and of saturated bromine vapour in a fused quartz cell. The latter was about 4.5 cm. deep and of poor quality, the end plates not being accurately parallel. The maximum ultra-violet transmission of this filter is near 275  $\mu\mu$  and one-sixth of the light transmitted lay below 300  $\mu\mu$ , as determined by exposing a thermopile alternately behind glass and quartz plates.

The spectral transmissions of these filters were determined in the usual manner by means of a spectrometer-thermopile-galvanometer combination.

*Thermostat.*—This was of simple construction. In the square ends of an open copper box, 10  $\times$  10  $\times$  5.2 cm., directly opposed central holes of 2.9 cm. diameter were cut. Around them, inside the box, was soldered a copper U, reaching to the top of the box and dividing it into two compartments. The circular apertures in the inner jacket were covered with quartz plates. This inner compartment held the reaction cell during insolation and was filled with distilled water. The outer jacket contained ice or water, depending on the temperature of the experiment which was 21°

unless otherwise stated. The temperature of the thermostat could readily be controlled by addition by hand of small quantities of hot water or of ice. A small heating coil was sometimes used.

*Energy Measurement.*—This was done by means of either a 1-cm. or a 2-cm. Moll thermopile (previously calibrated against a standard Hefner candle), the *E.M.F.* generated being measured by means of a potentiometer (Cambridge Instrument Company) and a moving-coil galvanometer (Gambrell). The over-all sensitivity was about  $5 \times 10^{-7}$  volt. Care was naturally taken that the whole of the beam under measurement fell directly on the surface of the thermopile, and all necessary corrections were applied for reflexion losses at the different quartz-air and quartz-liquid surfaces. Measurements of incident energy made at the beginning and end of any reaction usually agreed to within 1–2%. Measurement of the absorbed energy during the reaction proved to be undesirable for various practical reasons, one of which was the effect of intermittent illumination (*q.v.*). Consequently, the absorbed energy, though sometimes determined at the end of a reaction, was usually calculated.

*Intensity Variation.*—This was normally effected by altering the size of the aperture in the diaphragm F (Fig. 2) or the position of the lens  $C_2$ . The beam being convergent, the intensity was smaller the closer the lens to the cell and thermopile. In some cases, the average, as opposed to the true, intensity was varied by the use of an electrically driven rotating sector of variable aperture, running at a high speed (20–25 interruptions per sec.) and placed close to the aperture F, between it and  $C_2$ .

*Variation of Duration of Insolation.*—As it was found that, under certain conditions, the rate of the photolysis was proportional to the square root of the light intensity, it became desirable to carry out experiments under conditions of slowly intermitted radiation. The same sector, rotating with constant aperture, was used for this purpose, its rate of rotation being controlled by a simple gearing interposed between sector and motor, and consisting of six two-step pulleys rotating freely on one of two parallel stationary axes, and coupled with one another by suitable belting. The radii of the two steps in each pulley were in the ratio of 4:1. By changing the number of pulleys in use and suitably connecting them together, the sector speed could thus be varied between the extremes of  $1/4$  and  $1/4000$  of the speed resulting when motor and sector were directly coupled together. Alteration of the speed of the motor by a series resistance allowed of finer adjustments. In actual use, the maximum duration of a single light-period was 100 secs. In these experiments, the diaphragm F, with its immediately adjacent sector,



and the reaction cell G were so arranged as to be at conjugate foci of the lens  $C_2$ . This ensured that, at any particular point in the photolyte, the cut-off or switch-in of the light intensity was sudden and not gradual.

*Concentration Variation.*—Starting with the most concentrated solution, this was carried out by one of two methods, *viz.*, (i) replacement of some of the solution in the cell by distilled water; (ii) decomposition of some of the peroxide by insolation. The water used was made from ordinary laboratory distilled water by redistilling it from alkaline permanganate, passing the steam successively through a hot solution of potassium hydrogen sulphate, a 6-inch column of glass wool, and two trap-bulbs, and finally condensing it in a silica condenser and storing in a large waxed glass flask, sealed with a waxed glass plate. When the second method of dilution was used, the reaction cell was simply placed a few inches in front of the unscreened mercury arc and insolated for 24–48 hours. As already mentioned, this had the effect of destroying the fluorescent impurity in the perhydrol.

The concentrations of the various solutions were determined by titration with permanganate. For concentrated solutions, a 1-c.c. silica pipette was used and *N*-potassium permanganate; for the more dilute solutions, heavily waxed glass pipettes and permanganate solutions as dilute as 0.01*N* were employed. All concentrations are expressed as g.-mols. of hydrogen peroxide per litre.

*Temperature Coefficients.*—These were measured by carrying out a series of determinations with the thermostat adjusted at various temperatures from 2° to 26°, the limits being determined by the magnitude of the thermal reaction with the particular peroxide solution under examination. In order to avoid condensation of moisture on the surface of the front quartz window of the thermostat during measurements at low temperatures, a wide tube about 3" long, containing a small amount of phosphoric oxide and closed by a quartz plate, was firmly cemented on the front surface of the thermostat. This effectually prevented any condensation trouble.

*Experiments with Dilute Solutions.*—Several such series were studied. With the full light of the lamp, or chlorine-filtered light, a cell was used consisting of quartz plates sealed on by paraffin wax to a glass frame 5 mm. thick, through which a circular central cavity had been cut. The internal glass surface of this cavity was coated with paraffin wax, and a hole drilled into it from the edge of the frame allowed of filling and withdrawing of samples for titration. When 365  $\mu$  light was used, in order to shorten the experiment, the cell consisted of a small quartz flask immersed in a metal box, through which a rapid stream of tap water flowed, provided on

opposite sides with windows consisting of plates of Corning Glass G. 586 A.W. (see p. 602). A mercury arc was placed 10 cm. away from either window, and thus a reasonable rate of decomposition was secured. The reaction was followed in one case by titration, in others by measuring the oxygen given off under atmospheric pressure conditions. The latter procedure was capable of a fair degree of accuracy, as the runs were long, owing to the small amount of light absorbed, and the degree of supersaturation of oxygen could be kept so low as not to affect the results appreciably. In all cases where titration methods were used, the upper portion of the cell was blackened over, so that the surface insolated might remain constant throughout the run.

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## LXXXII.—*The Photolysis of Aqueous Hydrogen Peroxide Solutions. Part II. Experimental Results.*

By ARTHUR JOHN ALLMAND and DERRICK WILLIAM GRAHAM STYLE.

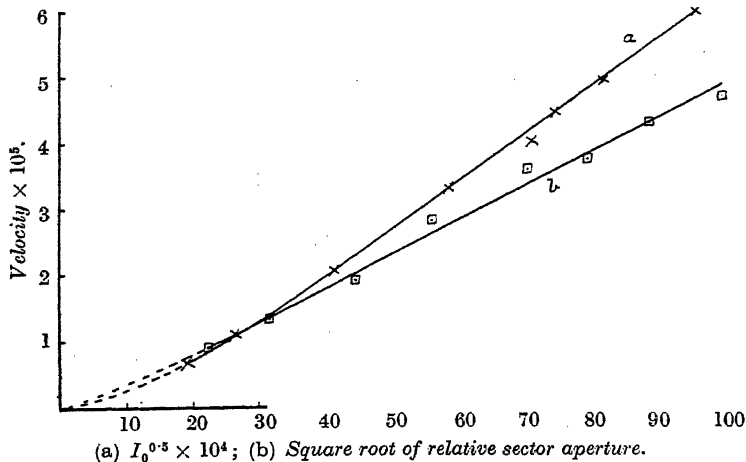
### *A. Experiments with Merck's Perhydrol.*

*Effect of Intensity and of Intermittent Illumination.*—These measurements were all carried out on undiluted perhydrol (about 10*M*). Curve *a*, Fig. 1, shows the results of true intensity variation with a beam of 365  $\mu$  light. Intensity is expressed as cal./cm.<sup>2</sup>/sec., and velocity as g.-mols. decomposed per hour. The total area irradiated at the front of the cell was 5.6 cm.<sup>2</sup>, and the time of reaction was 1–3 hours. Above a certain minimum intensity, the velocity is seen to be proportional to  $I_0^{0.5}$ . This unexpected result led us to undertake measurements in which the average intensity was altered by varying the aperture of a rapidly rotating sector between the limits of 5 and 100% of its full value. The data obtained, shown in Curve *b*, Fig. 1, are seen to be of the same general nature as with true variation.

The existence of the square-root relation between velocity and intensity suggested the formation in light of a catalyst acting analogously to iodine atoms in the iodine–potassium oxalate reaction (Berthoud and Bellenot, *J. Chim. physique*, 1924, 21, 308), and the matter was investigated further by the method of Briers, Chapman, and Walters (J., 1926, 562), a rotating sector of constant aperture but of variable rate of rotation being used. It was necessary to lower very considerably the speeds initially used before any effect was noticed, and the velocity only began to fall off when the duration

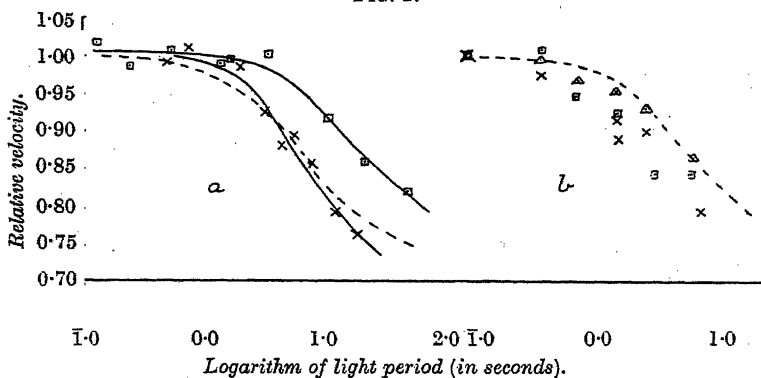
of a single light (or dark) period had risen to about 1 sec. It was still decreasing when the illumination period had reached 51 secs. The results of two such experiments, carried out with rather different

FIG. 1.



and unmeasured intensities, are plotted in Fig. 2a. The broken line represents the theoretical curve plotted for a catalyst of life of 1 sec., calculated from the formula of Briers, Chapman, and Walters, whilst

FIG. 2.



the horizontal line gives the velocity for the same continuously acting intensity (*i.e.*, half the velocity observed in absence of the sector).

Experiments on direct (true) intensity variation were next carried out with chlorine-filtered light ( $256 \mu\mu$ ). The results (Table I)

show plainly that, for light of this wave-length, under the prevailing experimental conditions, velocity ( $v$ ) is directly proportional to absorbed intensity ( $I$ ). As, however, the results with 365  $\mu\mu$  light suggested proportionality between velocity and intensity at low

TABLE I.

$I \times 10^5$ ...	8.0	13.7	15.1	16.9	23.1	29.2	34.4	39.0
$v \times 10^5$ ...	0.805	1.42	1.53	1.78	2.46	2.96	3.44	4.10
$v/I$ .....	1.01	1.03	1.01	1.05	1.06	1.01	1.00	1.05

intensities, it seemed possible that, with 256  $\mu\mu$  light of very high intensity, the  $I^{0.5}$  relation might hold. The limit to the direct measurement by the thermopile of the absorption of the complex beam of chlorine-filtered light had already been reached. As, however, with 365  $\mu\mu$  light, variation of true and of average intensity had given the same type of result, it was decided to do experiments with 256  $\mu\mu$  light of high intensity, using a rapidly rotating sector to control the average intensity of the beam. The results are contained in Table II. The velocity measured with the smallest sector opening was very near to the *maximum* velocity observed during the experiments recorded in Table I.

TABLE II.

Relative sector opening .....	1	2	4
$v \times 10^5$ .....	3.86	7.2	11.3
Ratio .....	3.86	3.6	2.83

It may be mentioned that the limiting values of  $\gamma_{365}$  actually obtained in the experiments plotted in Curve  $a$  (Fig. 1) were about 4.6 and 13.5 and would, of course, have been still higher at lower intensities, whilst the constant value of  $\gamma_{256}$  corresponding to the data in Table I is about 5.7. This last solution was submitted to a single experiment with 365  $\mu\mu$  light, and proved to be just twice as reactive at the same incident intensity as the solution used in the experiments of Curve  $a$ , Fig. 1. At all ordinary intensities, then,  $\gamma_{365}$  exceeds  $\gamma_{256}$  for concentrated perhydrol.

*Effect of Concentration.*—The first series of measurements was carried out with 365  $\mu\mu$  light, the concentration of the perhydrol, initially 12.10*M*, being altered in steps by the addition of distilled water until it had fallen to 1.11*M*. The thermal reaction velocities were determined and subtracted from the total velocities in light in order to obtain the net light velocity, and the absorbed energy was measured. Table III contains the results,  $v_d$  being the dark and  $v_{365 \mu\mu}$  the light velocity, both as mols./hr., and  $\gamma$  the quantum efficiency. The net light velocity (the table contains the results of successive duplicate experiments) rises to a maximum and then

TABLE III.

Conc.	$v_d \times 10^5$ .	$v_{365 \mu\mu} \times 10^5$ .	$\gamma$ (mean).	Conc.	$v_d \times 10^5$ .	$v_{365 \mu\mu} \times 10^5$ .	$\gamma$ (mean).
12.10	0.13	8.82	9.52	4.57	0.43	11.83	20.1
		8.91		2.20	0.75	9.05	22.1
9.06	0.39	11.75	14.8			9.50	
		11.86		1.11	0.71	5.69	23.4
6.92	0.35	12.38	16.6			5.61	
		12.52					

falls off as the solution is diluted,  $\gamma$  increases steadily throughout, and the thermal reaction velocity also increases with dilution, at all events over the greater part of the concentration range covered. The square of the quantum efficiency, when plotted against concentration, follows an equation of the type  $\gamma = (k_1 - k_2[\text{H}_2\text{O}_2])^{\frac{1}{2}}$ .

This remarkable increase of  $\gamma$  with dilution was quite unexpected, and it was thought that some positive catalyst had perhaps been introduced with the water used for dilution. A similar series was therefore carried out in which the dilution was effected by decomposing part of the peroxide by insolation as already described in Part I, measurements of velocity of decomposition being made both in 365  $\mu\mu$  and in 256  $\mu\mu$  light after each concentration change. It was at this stage that we first noticed the destruction of the fluorescent properties of the perhydrol as a result of prolonged irradiation. About 24 hours' insolation was required for effecting the first change in concentration (from 10.24 to 7.92M) and, as will be seen from Table IV, which contains the results of this series, the disappearance of the fluorescence was accompanied by a marked rise in the velocity of the thermal reaction, and by a decided fall in the photochemical reaction rates. Omitting the figures given by the most concentrated solution as not being comparable with the remainder, it will be seen that the results, as far as 365  $\mu\mu$  light is

TABLE IV.

Conc.	$v_d \times 10^5$ .	$v_{256 \mu} \times 10^5$ .	$v_{365} \times 10^5$ .	Relative $\gamma_{365}$ .
10.24	0.32	5.74	31.44	—
7.92	0.63	4.76	18.96	1.00
6.90	0.67	4.82	20.22	} 1.30
		5.00	24.30	
4.65	0.51	7.04	26.38	} (mean) 2.11
		7.12		
1.44	0.30	6.50	21.32	4.92

concerned, are qualitatively similar to those given by the fluorescent solution used in the first series (Table III). Further, the velocity with the chlorine-filtered light increases in the same way with dilution, passes through a maximum and falls off, the quantum efficiency altering in the same manner, absorption always being

complete. The thermal velocity, however, decreases with increasing dilution, whereas, in the fluorescing solution, it rises.

The results being obviously irregular, a similar set of experiments was carried out, after the fluorescence had been destroyed by a preliminary insolation. The same general type of result was obtained, but in detail the figures were as erratic as before. Finally, the original method of dilution with distilled water was reverted to, the fluorescent impurity again being destroyed at the commencement of the experiment. The readings were carried to concentrations as low as 0.06 and 0.02*M*, with 365  $\mu\mu$  and 256  $\mu\mu$  respectively, and the results are contained in Table V and in Fig. 3.\* They confirm the former series in all essential points.

TABLE V.

Conc.	$v_d \times 10^5$	$v_{256 \mu\mu} \times 10^5$	$v_{365 \mu\mu} \times 10^5$	Relative $\gamma_{365}$
9.52	1.02	8.08	46.56	1.00
7.54	1.18	8.26	46.20	1.17
4.95	1.04	9.30	53.84	1.89
2.79	0.99	9.46	52.96	3.06
1.39	0.70	10.72	50.75	5.55
0.671	0.66	10.76	25.68	5.67
0.201	0.28	12.70	14.08	9.93
0.060	0.16	15.04	3.56	7.94
0.021		11.16		

*Temperature Coefficient.*—This was determined for the concentrated perhydrol and for the 365  $\mu\mu$  line only. Measurements were made at 11°, 14.5°, 21°, and 26°, and the thermal reaction velocity was roughly measured at 21° and 31°. The latter had a temperature coefficient of about 2.1 (no precise significance is attached to this figure), and at 21° accounted for 3% of the total reaction. From the smoothed curve passing through the plot of the corrected light velocities, a value of 1.39—1.40 was read off for the photochemical temperature coefficient.

#### B. Experiments with Hydrogen Peroxide prepared in the Laboratory.

The totally unexpected nature of the relations observed when using high light intensities and high concentrations of perhydrol made it very desirable to repeat the work with a material definitely free from any substance, such as the fluorescent impurity or its decomposition products, which might conceivably affect the results. Experiments were therefore carried out with hydrogen peroxide prepared ourselves by the method already described.

*Preliminary Experiments.*—These were done essentially in order

\* In Figs. 3, 4, and 8, the various graphs for relative quantum efficiency are in no sense comparable with others on the same diagram, each being plotted on its own arbitrary scale along the ordinate.

to confirm or otherwise the effect of concentration change noted above. Commencing with concentrated peroxide, and then working with weaker solutions prepared by dilution with water, the light velocities were determined for the  $365\text{ }\mu$  line and for light transmitted by the chlorine-bromine filter ( $275\text{ }\mu$ ). At the same time, as the thermal velocities were now sufficiently high, they also were accurately determined. The results are contained in Table VI, and in Fig. 4 are plotted, as functions of concentration, the relative

FIG. 3.

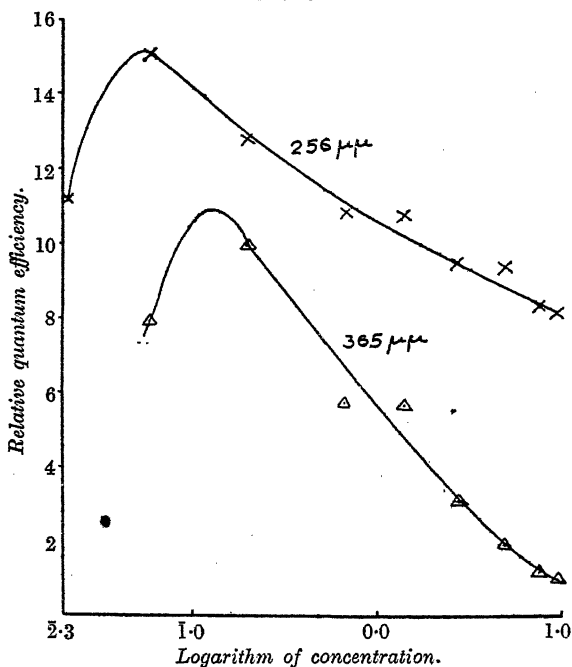


TABLE VI.

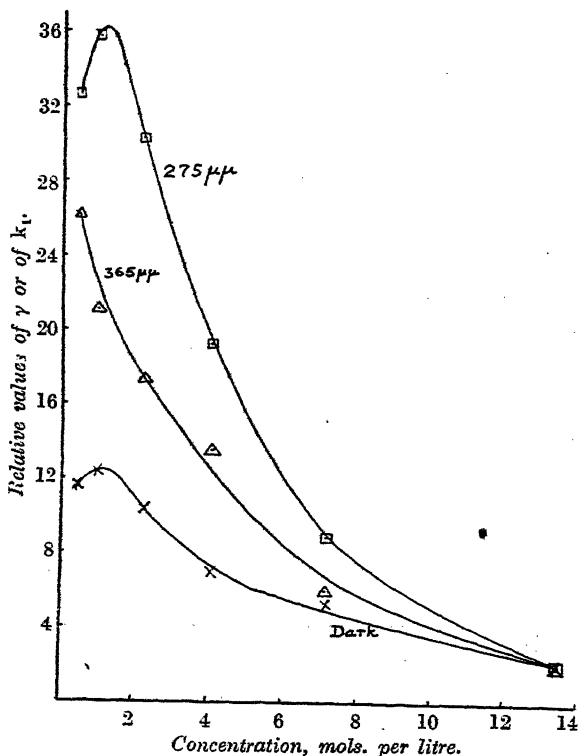
Conc. ....	13.44	7.19	4.04	2.21	0.98	0.475
$v_d \times 10^5$ .....	0.98	4.65	5.70	4.89	2.56	1.13
$v_{365\text{ }\mu} \times 10^5$ .....	17.66	69.7	98.8	74.0	41.4	25.6
$v_{275\text{ }\mu} \times 10^5$ .....	2.38	12.31	16.36	24.60	29.16	27.42

quantum efficiencies for the light reactions and the unimolecular thermal reaction velocity coefficient (*i.e.*, rate of decomposition per unit mass of peroxide). The results are similar to the former ones in general outline (the continued rise of  $\gamma_{365}$  appears, in the light of other data, to be perhaps due to experimental error).

*Effect of Concentration, Wave-length, and Intensity on Quantum Efficiency.*—Two systematic series of experiments were undertaken.

In the first, an 11.5*M*-solution was successively insolated with 365  $\mu$  light of a whole range of measured intensities, and then by light transmitted by the chlorine-bromine filter (275  $\mu$  region), a series of different intensities again being used. The solution was then diluted by addition of water to 5.45*M*, and insolated in a similar fashion, the whole process being repeated for concentrations of 2.45, 1.19, and 0.48*M*. The second series resembled the first,

FIG. 4.



except that beams of 365  $\mu$  and 307  $\mu$  (average) light were employed, the concentrations being 10.17, 6.05, 3.69, 1.92, 0.95, and 0.62*M*. The reason for not investigating the action of the three wave-lengths on the same solution was the necessity of minimising the changes in concentration caused by the photodecomposition. Just as in the measurements already described, no great accuracy is claimed for the figures, owing to certain disturbing factors imperfectly controlled (four experiments in the second series have been neglected on this account), nor are the absolute values of any



particular interest, in view of the whole nature of the reaction. Table VII contains typical specimens of the experimental data. In all cases, the area illuminated by the incident converging beam was 5.6 cm.<sup>2</sup>. Col. 1 gives the intensity in terms of incident quanta/hour/cm.<sup>2</sup>  $\times 10^{-18}$ , col. 2 the total quanta absorbed per hour  $\times 10^{-18}$ ; and col. 3 the total molecules of peroxide decomposed per hour  $\times 10^{-19}$ .

FIG. 5.

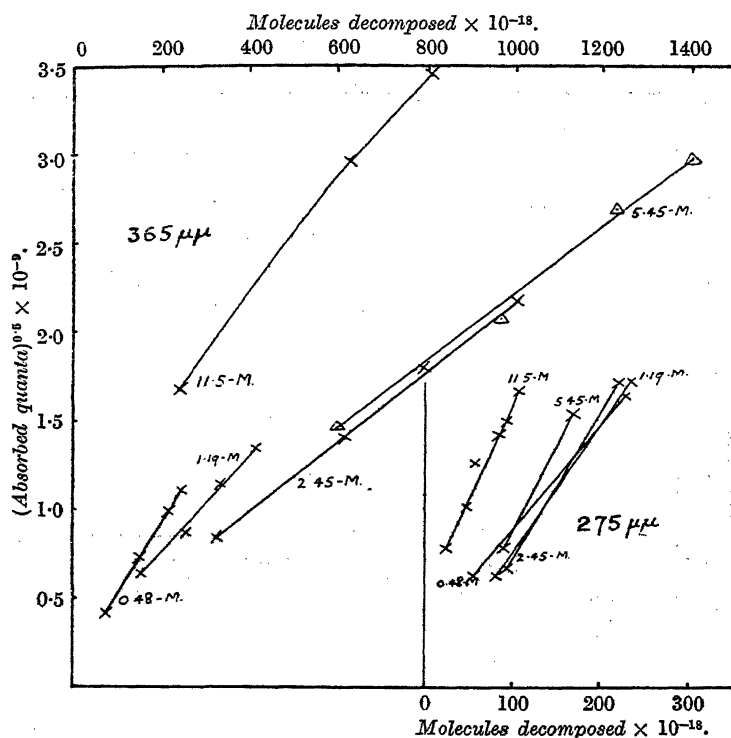


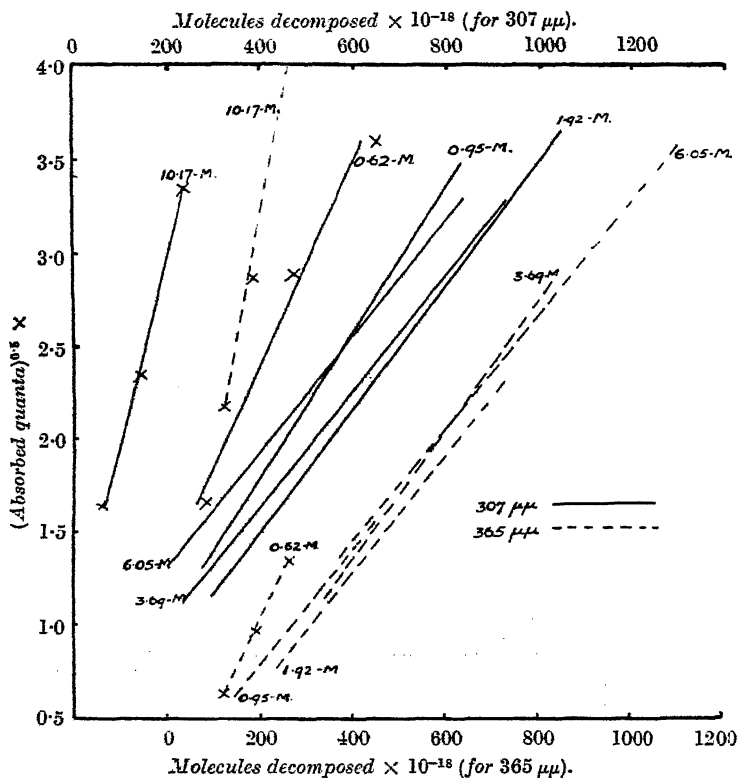
TABLE VII.

(a) Series I. 275 $\mu\text{m}$ ; 1.19M-H <sub>2</sub> O <sub>2</sub> .			(b) Series II. 365 $\mu\text{m}$ ; 3.69M-H <sub>2</sub> O <sub>2</sub> .		
(1).	(2).	(3).	(1).	(2).	(3).
0.0684	0.383	7.40	0.902	1.23	33.9
0.165	0.927	12.5	1.56	2.13	42.5
0.259	1.47	17.7	4.23	5.75	75.8
0.412	2.31	19.6	5.63	7.56	82.4
0.531	2.97	23.6	5.88	7.99	78.9

The results as a whole are shown in Figs. 5 and 6, where the square root of the number of quanta absorbed per hour is plotted

against the number of molecules decomposed per hour. In order not to confuse the diagrams, the actual experimental points in many cases are not put in, but merely the best line drawn through them. Further, in both diagrams, and in order to economise space, the curves for  $365\ \mu\mu$  light and for the most concentrated peroxide solution are not completely shown. It will be obvious that the quantum efficiency for any particular concentration and rate of

FIG. 6.



energy absorption can be read off by dividing the abscissa by the square of the ordinate.

It will be noticed that, with one exception, *viz.*,  $11.5M$ -peroxide and  $365\ \mu\mu$ , the curves are linear. Although it will appear later that, in one or two cases, this linearity is only apparent and due to experimental error and the scale of plotting, we are nevertheless justified in concluding that, in general, over our working range of concentration and intensity, any increase in velocity is proportional

to the corresponding increase in the square root of the intensity, whatever the wave-length of the light. It will further be noticed that the majority of the curves, if produced, do not pass through the origin, but cut the ordinate. This fact is reminiscent of Curve *a* (Fig. 1); its significance will be discussed later.

With regard to the relative values of the quantum efficiencies obtained at any given rate of absorption of quanta, it will be seen (a) that, in general,  $\gamma_{365}$  is greater than  $\gamma_{307}$  and  $\gamma_{275}$ ; (b) that the  $\gamma_{365}$  values are considerably higher in Series I (Fig. 5) than in Series II (Fig. 6); (c) that, as the concentration falls,  $\gamma$  increases in every case, and usually passes through a maximum at some intermediate concentration and falls off in dilute solution. Conclusions (a) and (c) are in accordance with the results obtained with perhydrol insolated by 256  $\mu\mu$  and 365  $\mu\mu$  light. The absolute values of  $\gamma$  naturally vary between wide limits, roughly 20–500, depending on wave-length, intensity, concentration, and the particular solution used.

*Effect of Intermittent Illumination.*—It was clearly desirable to see whether the "pure" hydrogen peroxide solutions behaved in the same manner as did perhydrol during intermittent insolation with light and dark periods of varied length. Measurements were done with 307  $\mu\mu$  light, a new cell with well-annealed surfaces being used, together with a temperature of 2° so as to minimise thermal decomposition. Three concentrations were employed, viz., 11.0, 6.4, and 3.3*M*. The method of experimentation was as already described, the duration of a single reaction always extending over at least 100 intermissions. The data are contained in Fig. 2*b*, where the broken line again represents the theoretical curve for a mean life of 1 sec., whilst the horizontal line denotes the decomposition for the same continuous intensity. The results are clearly subject to considerable error, but suffice to show that the mean life of the presumed catalyst rises with dilution and is about 0.4 sec. for 11*M*-solutions. No exact comparison between Figs. 2*a* and 2*b* can be made, for the light intensities used were not measured, whilst the solutions were of different origin. It would seem likely, however, that the mean life of the catalyst increases with the wave-length of the active light.

*Temperature Coefficients.*—These were determined for three concentrations and for three wave-lengths, two measurements being made at each temperature, viz., 2° and 22°. The temperature coefficient of the thermal reaction was necessarily measured at the same time. The results are contained in Table VIII, from which it would appear that any effect of concentration is within the limits of experimental error.

TABLE VIII.

Conc.	Temperature coefficients.			
	Thermal.	365 $\mu$ .	307 $\mu$ .	275 $\mu$ .
10.5 <i>M</i> .....	2.96	1.43	1.35	1.26
7.3 <i>M</i> .....	2.66	1.39	1.38	1.28
1.3 <i>M</i> .....	2.87	1.45	1.40	1.29
Mean values .....	2.83	1.42	1.38	1.28

Previous results for the photochemical reaction are as follows, T.C. denoting the temperature coefficient :

Worker.	T.C.	Conditions of experiment.
Tian	1.15	Thin layers of dilute perhydrol. Centre of gravity of absorbed light probably 260 $\mu$ .
Kornfeld	1.32	Dilute solutions of perhydrol. Uviol glass apparatus. Light chiefly absorbed 313 $\mu$ .
Matthews and Curtis	1.5	Uviol lamp radiation passed through several thicknesses of Uviol glass. Dilute perhydrol. Active light probably chiefly 365 $\mu$ . Thermal reaction not corrected for.
Anderson and Taylor	1.43	Pure dilute solutions. Full light of quartz mercury lamp in quartz vessels.

Our value for concentrated perhydrol and 365  $\mu$  was 1.39—1.40.

### C. Experiments with Dilute Solutions.

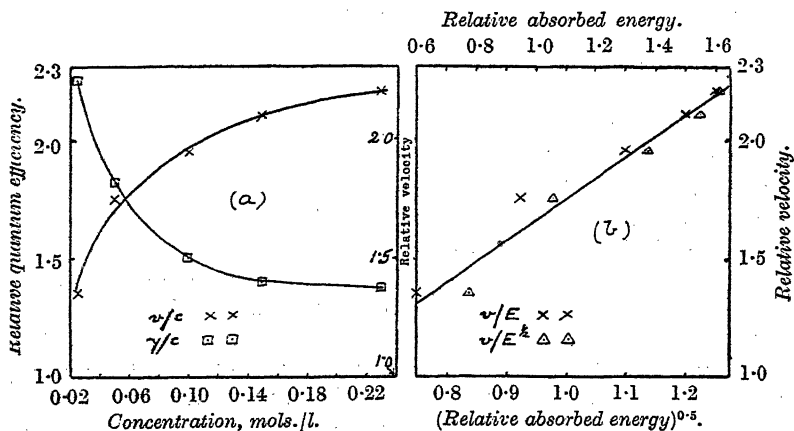
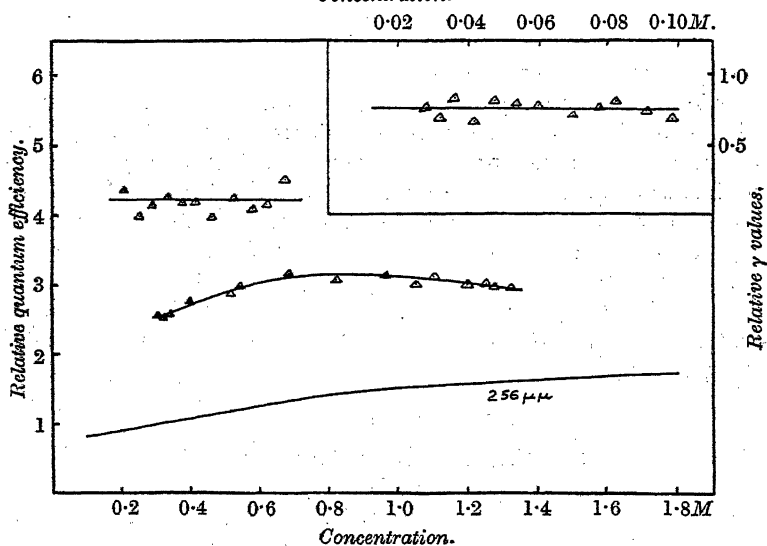
One of the most striking of the results recorded in sections A and B is the passage of  $\gamma$  through a maximum as the peroxide concentration is increased. It was clearly desirable to investigate rather more fully the behaviour of solutions of low concentration, particularly in view of the statement frequently made that the reaction is of the first order.

Some of our earliest experiments, carried out on dilute solutions of Merck's peroxide containing a nitrogenous inhibitor, were of this nature, the 5-mm. wax-lined cell (described at the end of Part I) being used, and the initial rates of reaction of a series of solutions of different concentrations being measured both in the full light of the lamp, and also in light which had been passed through a 2-cm. chlorine filter. They gave the same type of velocity-concentration curve. The results obtained with the chlorine-filtered light are shown in Figs. 7*a* and 7*b*. The former contains, plotted against concentration, the relative measured velocities and the relative quantum efficiencies, these being calculated from a knowledge of the energy distribution in the filtered beam and the extinctions of the different solutions. Fig. 7*b* shows the velocity plotted against (a) the light absorption, (b) the square root of the light absorption. Although the points are irregular, the best straight line drawn through the latter set passes through the origin on being produced.

A similar experiment (5-cm. chlorine-filter; 256  $\mu$ ) was carried

out on a dilute solution of the pure peroxide, which was initially 1.8M and decomposed during the insolation down to a final concentration of 0.1M. Here the behaviour was quite different,  $\gamma$

FIG. 7.


 FIG. 8.  
Concentration.


dropping throughout as the concentration fell (Fig. 8). Above 0.3M, absorption of the active light was practically complete. The curve has been drawn from the smoothed experimental data.

Finally, a number of experiments were carried out with dilute

solutions of the pure material and 365  $\mu\mu$  light, using the methods described at the end of Part I and following the reaction by measuring the evolved oxygen. The relative quantum efficiencies for three such experiments, calculated by dividing the velocities by the average concentration between each pair of points, are shown in Fig. 8. No very definite conclusion can be drawn from them and the experiments clearly need extension.

#### D. Summary of Experimental Results.

Figs. 5 and 6 exhibit the results of two comprehensive series of experiments in which the effects of variations in  $\lambda$ ,  $I_0$ , and  $[\text{H}_2\text{O}_2]$  on the photolysis were investigated, specimen detailed figures being tabulated in Table VII. In the majority of cases, the observed velocity can be plotted, within the limits of experimental error, linearly against the square root of the rate of absorption of energy, the curves appearing, when produced, either to pass through the origin or to cut the energy axis. Experimental error and the scale of plotting both forbid their closer analysis, which is best achieved by calculating from the original data relative values of the characteristic  $k_A$  constants (J., 1929, 1557) by means of the formula

$$-\Delta u = k_A \cdot I_0^{\frac{1}{2}} \cdot \frac{2}{\alpha^{\frac{1}{2}} c^{\frac{1}{2}} l} \cdot (1 - 10^{-\frac{1}{2} \alpha c l})$$

where, in the present case,  $-\Delta u$  is the number of molecules of peroxide decomposed per hour,  $I_0$  the total number of quanta incident per hour per  $\text{cm}^2$  on the illuminated area of the cell,  $c$  the concentration in mols./litre,  $\alpha$  the average extinction coefficient for the incident light, and  $l$  the depth of the cell (5 cm.). With the exception of four readings in Series II, which were clearly in serious error, all the data have been calculated in this way, the extinction coefficients used being 0.0066 for 365  $\mu\mu$ , 0.59 for 307  $\mu\mu$ , and 6 for 275  $\mu\mu$ . For the 275  $\mu\mu$  experiments, and for all but the two weakest solutions with the 307  $\mu\mu$  light, the term  $1 - 10^{-\frac{1}{2} \alpha c l}$  is practically unity, the expression simplifying to

$$-\Delta u = 2k_A I_0^{\frac{1}{2}} / c^{\frac{1}{2}} x^{\frac{1}{2}}.$$

Table IX contains in detail the values of  $k_A \times 10^{-11}$  calculated from the readings of Series I with 275  $\mu\mu$  light, arranged in each case in order of ascending values of  $I_0$  (not given; they varied between limits of 0.068— $0.531 \times 10^{18}$  quanta/hour/ $\text{cm}^2$ ).

The constancy of the  $k_A$  values for the three intermediate concentrations indicates that, over the whole intensity range covered, except for the lowest intensity with the 1.19M-solution, the velocity is proportional to  $I_0^{0.5}$ . This relation clearly does not hold either

TABLE IX.

 Values of  $k_A \times 10^{-11}$ .

11.5M.	5.45M.	2.45M.	1.19M.	0.48M.
3.20	7.51	5.79	(3.77)	1.92
4.77	7.55	6.04	4.11	2.34
5.00	7.93	5.30	4.65	2.57
5.86	7.36	6.89	4.08	3.16
6.22		5.07	4.33	
6.43		5.44		
Means —	7.59	5.92		

for the weakest or for the strongest solution, and reference to Fig. 9 shows that the  $I_0$  rule is obeyed by the 11.5M-solution and possibly by the 0.48M-solution (points very scattered).

FIG. 9.

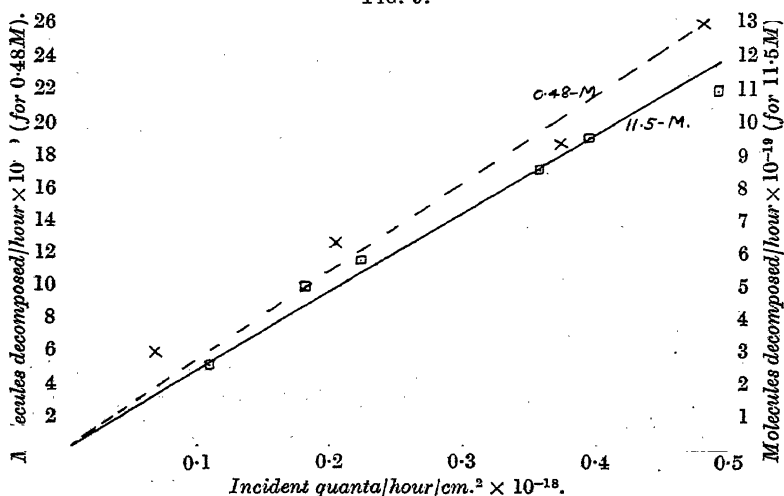


Table X contains a summary of all the results in the form of the mean values of  $k_A$  holding for any particular wave-length and concentration. In two further cases with concentrated solutions, apart from that just mentioned, the values were found to drift, as the intensity was raised, in a direction which showed that the  $I_0^{0.5}$  rule was breaking down at low intensities, and being replaced by the  $I_0$

TABLE X.

Series I.			Series II.		
[H <sub>2</sub> O <sub>2</sub> ].	275 $\mu\mu$ .	365 $\mu\mu$ .	[H <sub>2</sub> O <sub>2</sub> ].	307 $\mu\mu$ .	365 $\mu\mu$ .
11.5M	3.20 → 6.43	1.01 → 1.91	10.17M	1.13 → 2.08	0.42
5.45	7.59	(2.86)3.28		5.85	2.09
2.45	5.92	(2.72)3.13		4.97	2.13
1.19	(3.77)4.29	(1.72)2.12		3.61	2.21
0.48	1.92 → 3.16	(1.32)1.61		2.09	1.93
				1.38	1.43

rule. In addition, in Series I with  $365\text{ }\mu\mu$  light, the  $k_A$  values obtained with the lowest intensity used (figures in brackets) were always lower than those subsequently found, indicating again that the  $I_0^{0.5}$  rule was not being fully obeyed under such conditions.

Taking into account the various differences manifested in the above tables, we can summarise the main results of our experimental work as follows:

(1) Over wide ranges of  $I$ ,  $\lambda$ , and  $[\text{H}_2\text{O}_2]$ , the rate of photolysis is proportional to  $I_0^{0.5}$ . This behaviour is favoured by high intensities (Fig. 1, Tables II, IX, X); with low intensities, a tendency towards a reaction of the  $I_0$  type becomes apparent. At very high and at low concentrations (Fig. 9; Tables IX, X; also previous results of Tian and of Henri and Wurmser, *loc. cit.*), the velocity tends to be proportional to the intensity.

(2) The velocity at constant incident intensity passes through a maximum as  $[\text{H}_2\text{O}_2]$  is increased and then falls off (Tables III, IV, V, VI).

(3) In some cases,  $\gamma$  also passes through a similar maximum with increase in  $[\text{H}_2\text{O}_2]$  (Tables IV, V; Figs. 3, 4, 5, 6, 8). This is not always the case in the concentration range studied (Tables III, IV; Figs. 4, 5, 8).

(4) Under our experimental conditions  $\gamma$  tends to be high; there is a catalytic chain with a life of about 1 sec., becoming less with increase in concentration and probably also with increase in frequency (Fig. 2).

(5) Both  $\gamma$  (tables and diagrams) and temperature coefficient (Table VIII) under the prevailing conditions fall off as the frequency of the light is increased, the temperature coefficient doing so to an extent independent of concentration.

(6) A dilute solution of hydrogen peroxide containing inhibitor decomposes with a velocity which rises with increase in concentration at a rate proportional to the square root of the rate of the absorption of energy (Fig. 7).

(7) The velocity of thermal decomposition of peroxide solutions passes through a maximum and subsequently falls off as  $[\text{H}_2\text{O}_2]$  increases. In one case (Fig. 4), the corresponding unimolecular velocity coefficient-concentration curve also has a maximum; other data (Tables IV, V) give no such maximum. The temperature coefficient of the rate of thermal decomposition is normal, and is independent of  $[\text{H}_2\text{O}_2]$  over the concentration limits tested (Table VIII).

#### E. Discussion.

To explain these very complex relations (many of them unexpected, *e.g.*, the effect of intensity in the intermediate concentration



range, the relations between  $\gamma$  and  $\lambda$  and between  $[\text{H}_2\text{O}_2]$  and velocity) on a simple basis is clearly impossible, and we shall at present confine ourselves to a brief discussion of some of the more salient points.

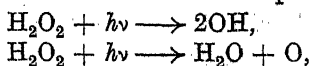
(i) Any satisfactory theory of the photolysis of hydrogen peroxide solutions must first of all take into account the great similarity between the photochemical and thermal reactions. This is apparent throughout, and particularly so in Table VI, where, except for the lowest concentration employed, the thermal velocity and the velocity in  $365 \mu\mu$  light are practically proportional to one another within the experimental error.

(ii) The next point to emphasise is the effect of dust particles as demonstrated by the work of F. O. Rice and his collaborators. The photochemical, and hence presumably the thermal, reaction is a chain reaction, and the question arises as to whether it is the initiation or the continuation (or both?) of the chain which is a surface reaction. Recent workers (Williams, *Trans. Faraday Soc.*, 1928, 24, 245; Pana, *ibid.*, p. 486) on the thermal reaction conclude that it is initiated on the surface of the vessel or on dust particles.

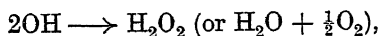
(iii) We find the temperature coefficients of the photolysis to decrease with increasing frequency, but to be independent of concentration. This strongly suggests that they are concerned with the primary process only. Calculating the molar energy of activation ( $E$ ) by the method of Arrhenius, we find  $E_{365 \mu\mu} = 5850$ ,  $E_{307 \mu\mu} = 5380$ ,  $E_{275 \mu\mu} = 4120$  cals. With Tolman (*J. Amer. Chem. Soc.*, 1923, 45, 2285), we can equate  $E$  to  $N(\bar{\epsilon} - \bar{\epsilon})$ , where  $\bar{\epsilon}$  represents the average energy of all molecules of peroxide and  $\bar{\epsilon}$  the average energy (before absorption) of those molecules which are sufficiently activated by quantum absorption to be capable of initiating a reaction chain. The fraction of molecules ( $f$ ) in this potentially reactive state ( $\bar{\epsilon}$ ) in respect of light of a particular wavelength will be given by  $e^{-E/RT}$ , from which we obtain  $f_{365 \mu\mu} = 4 \times 10^{-5}$ ,  $f_{307 \mu\mu} = 9 \times 10^{-5}$ ,  $f_{275 \mu\mu} = 80 \times 10^{-5}$ .

If this view is correct, it appears that only a very small proportion of the absorbing molecules react subsequently to absorption, and that therefore the reaction chains must be exceedingly long—of the order of  $10^4$  to  $10^7$  links, leaving out of account any deactivation (by whatever means) experienced prior to the inception of the chain.

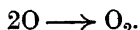
(iv) The  $I_0^{0.5}$  relation suggests that the catalyst (of mean life about 1 sec.) which is responsible for the reaction chain may consist either of hydroxyl groups or of oxygen atoms, produced in the liquid phase in accordance with one of the equations



and, when their rate of production per unit volume is sufficiently high, disappearing in accordance with either



or



Thermochemically, these two primary light actions are both possible, the former absorbing 56.5 Cals. (calculated from the work of Bonhoeffer and Reichardt, *Z. physikal. Chem.*, 1928, *A*, **139**, 75) and the latter 56.8 Cals. Referred to a single molecule, these figures correspond to a light quantum at about 500  $\mu$ , i.e., in the blue-green region of the spectrum, whereas the longest wave-length used by us was 365  $\mu$ .

(v) To account for the validity of the  $I_0$  relation at low intensities and concentrations, and also at high concentrations, additional hypotheses are necessary. For example, we have tested the assumption that, the hydroxyl group being the catalyst, it can be removed unimolecularly in certain circumstances by adsorption on dust particles, and, under other conditions, by combination with peroxide molecules to form unstable  $\text{H}_3\text{O}_3$  molecules which then rapidly react with one another. If the "chain" be supposed to be initiated by impact of such hydroxyl groups on the layer of peroxide molecules adsorbed on dust particles, and if a further type of "deactivating" collision involving peroxide molecules be introduced, then the majority of the experimental facts found by us can be brought into line. Some, however, remain unexplained. For example, the predicted behaviour of solutions of concentration 2*M* and less is not completely in accord with the (rather uncertain) experimental data, and further work is being done in this direction. Until the results of these experiments are available, it is of little use to discuss further either the explanation of our own results or their relation to the work of others.

(vi) Two particular points may be mentioned in conclusion.

(1) Our results with the dilute solution containing inhibitor (Fig. 7) can readily be explained on the mechanism referred to above.  
 (2) This point relates to the values for the empirical experimental constant  $k_A$ , contained in Table X. They vary with concentration, which merely shows at present that the photolysis is a complex one, but are also seen to rise with increasing frequency (see J., 1929, 1537) and not to decrease, as is the case with the values of  $\gamma$ . On the theory outlined above, they should be proportional to the square root of the coefficient ( $k_1$ ) which measures the efficiency of the primary dissociation process following on quantum absorption.

These  $k_1$  values are proportional to the  $f$  values calculated above, and we consequently have

$$(k_1)_{365\ \mu\mu} : (k_1)_{307\ \mu\mu} : (k_1)_{275\ \mu\mu} = 4 : 9 : 80$$

and hence

$$(k_A)_{365\ \mu\mu} : (k_A)_{307\ \mu\mu} : (k_A)_{275\ \mu\mu} = 2 : 3 : 9.$$

There is no quantitative coincidence between these ratios and the varying figures contained in Table X, but the fact that the admittedly incomplete theory gives even the found measure of agreement is of interest.

The experiments described in this and the preceding paper were carried out between October 1925 and April 1928. We are indebted to grants received from Brunner Mond and Company, Limited, and from Imperial Chemical Industries, Limited, which enabled us to purchase the electrical instruments, quartz cells, mercury lamps, and rotating sector used in the work. One of us (D. W. G. S.) wishes in addition to acknowledge the grant made to him by the Department of Scientific and Industrial Research whilst a student in training.

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### LXXXIII.—*The Angles of Floating Lenses.*

By CHARLES GEORGE LYONS.

SEVERAL investigations have been made on the relationships between the statical equilibrium of an interface and the arrangement of the molecules at the boundary. Many of these studies were based on measurement of angles of contact; for example, Adam and Jessop (J., 1925, 127, 1863) studied the variation in these angles for water against various solid substances which had been used in film experiments. Practically all of these earlier researches were concerned with the contact angles of liquids against solids, and the liquid-liquid angles have been comparatively neglected.

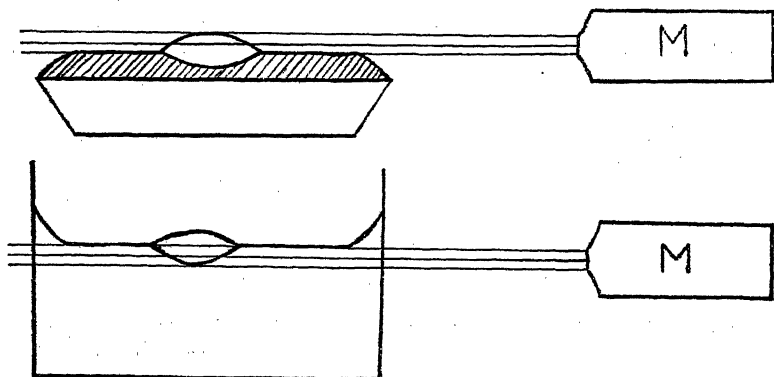
The exact configuration of the molecules at the surface of a solid cannot be established except in the case of a single crystal, but at a liquid boundary the molecular orientation presents much less difficulty. It seemed probable, therefore, that the measurement of liquid-liquid angles of contact would yield definite information about the molecular basis of the interfacial equilibrium. These angles are most conveniently obtained as the angles of a lens of one liquid which is floating on another liquid, both being mutually

insoluble. Such angles were studied qualitatively by Quincke (*Phil. Mag.*, 1871, **41**, 454) and by Hardy (*Proc. Roy. Soc.*, 1912, **A**, **86**, 61), and quantitatively by Coghill and Anderson (*Bureau of Mines Tech. Papers*, 1924, 262); the last two authors, however, used an indirect method, calculating the angle from the dimensions of the lens on the assumption that its shape was governed solely by the surface-tension forces acting at its edges. As this assumption need not necessarily be true, it was decided to investigate these angles by direct measurement.

#### EXPERIMENTAL.

A drop of a liquid was placed on the surface of another in which it was insoluble, and the floating lens formed was held loosely in position by a wire just touching its surface.

FIG. 1.



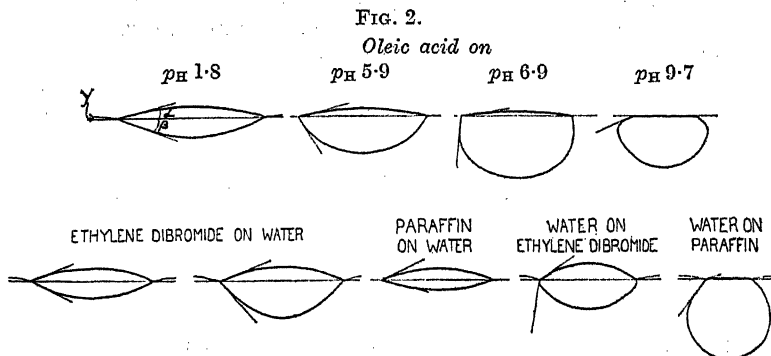
The surface of the liquid was illuminated with a horizontal beam of light, and the lens was then viewed with a microscope whose axis was horizontal. Its image was projected on a camera, and a photograph of the magnified image was taken. The angles of contact and all other data were then easily and accurately measurable on the photographic plate.

As the lens was illuminated parallel to the surface of the liquid on which it was floating, there was a possibility of distortion of the image by the meniscus at the walls of the containing vessel. This distortion was avoided (see Fig. 1) by photographing the upper surface of the lens in a trough filled nearly to overflowing so that the meniscus curved downwards, and the lower surface in a glass cell in which the meniscus was attracted upwards.

The apparatus, when finally adjusted, was tested for distortion by three methods: (1) a circular object held vertically in the surface

of the liquid and perpendicular to the direction of vision was found to give a circular image; (2) by means of a graduated scale it was shown that the magnification ratio was the same vertically and horizontally; (3) pieces of wire bent into known angles gave images bearing these angles. The experimental arrangement therefore gave images of the lenses which represented their true shape.

To obtain the angles of a given lens, the microscope was focused on a medial section, and the angles were measured on the photographic plate with a protractor. The values obtained were probably accurate to  $\pm 2^\circ$ , the value of  $\gamma$ , the angle formed by the meniscus of the supporting liquid (see Fig. 2), being the most difficult to obtain, as it was usually small.



With this apparatus, lenses of oleic acid on aqueous solutions of various  $p_H$  were studied; also lenses of ethylene dibromide, carbon tetrachloride, and nujol (medicinal paraffin) on water, and of water on the last three liquids. The angles made by the liquid boundaries at the edge of the lens with the horizontal are given in Table I, in which surface tensions are given in dynes/cm., and Fig. 2 contains

TABLE I.

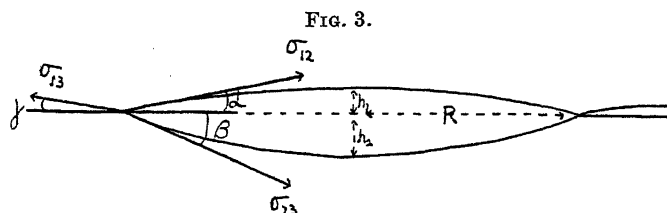
Liquid.	Lens.	$\alpha$ .	$\beta$ .	$\gamma$ .	$\sigma_{12}$ .	$\sigma_{23}$ .	$\sigma_{13}$ .
Water	Oleic acid	$10^\circ$	$20^\circ$	$0^\circ$	32.5	15.7	42.5
HCl, $p_H$ 1.8	"	13	28	2	32.5	16.0	44.5
* $p_H$ 5.9	"	13	57	0	32.5	11.7	41.0
* $p_H$ 6.9	"	7	96	0	32.5	9.7	35.0
* $p_H$ 9.7	"	Small	157	—	32.5	Small	34.0
$C_2H_4Br_2$	Water	34	99	4	73.0	36.5	38.7
$CCl_4$	"	28	99	—11	73.0	45.0	26.7
Paraffin	"	17	127	8	73.0	51.0	22.0
Water	$C_2H_4Br_2$	21	25—48	6—9	38.7	36.5	73.0
"	$CCl_4$	12	Variable		26.7	45.0	73.0
"	Paraffin	25	14	2	22.0	51.0	73.0

\* These solutions were obtained by the use of phosphate buffers.

diagrams of the shapes assumed by the lenses under different conditions. From these, it is seen that the shape can be varied within wide limits, the lower submerged surface being particularly sensitive to changes in the conditions. Alteration in the size of the lens within the diameter range 0.4—2.5 mm. caused no appreciable alteration in the angles.

### Discussion.

These results show that not only the shape but also the submergence of the lens changed when the surface tensions at the boundaries were varied. The fraction of the lens below the level of the surface of the bulk liquid ranged from 0.4 almost to unity for different pairs of liquids. The oleic acid series was especially interesting, for, as the underlying solution increased in alkalinity, the lens sank steadily into it, the lower surface becoming more and more curved and the value of  $\beta$  steadily rising.



The shape of the lens was shown in this way to be controlled chiefly by the interfacial tension between the two liquids. This tension gradually decreased from 16.0 dynes/cm. to a very small value as the alkalinity rose, while the individual surface tensions of the two liquids (against air) remained practically constant.

These results are qualitatively explicable on the simple theory of the lens equilibrium. This demands that the angles should be controlled solely by the surface-tension forces, in such a way that at the edge of the drop the three surface tensions are in statical equilibrium as shown by the triangle of forces (Neumann's triangle). These conditions may be written in the form of the two equations

$$\sigma_{12} \sin \alpha - \sigma_{23} \sin \beta + \sigma_{13} \sin \gamma = 0 \quad . \quad . \quad (1)$$

$$\sigma_{12} \cos \alpha + \sigma_{23} \cos \beta - \sigma_{13} \cos \gamma = 0 \quad . \quad . \quad (2)$$

where  $\sigma_{12}$  and  $\sigma_{13}$  are the surface tensions of the liquids (in air), and  $\sigma_{23}$  is their interfacial tension, the angles being as shown in Fig. 3. From these equations it will be seen that if the interfacial tension is decreased while the surface tensions remain nearly constant, the lower angle of contact,  $\beta$ , will gradually increase so that  $\sigma_{23} \sin \beta$  may still balance the vertical component of  $\sigma_{12}$ . This angle must

become re-entrant if the horizontal component of the surface tension of the lens liquid becomes greater than that of the supporting liquid. The observed changes in the oleic acid lenses as the interfacial tension is progressively decreased are in agreement with these predictions.

The increased submergence of the lens as the interfacial tension decreases follows directly from considerations of the free energy of the system. As the interfacial tension decreases, the surface energy at the liquid-liquid boundary decreases, and the area of this interface must increase at the expense of the other surfaces. This effect is analogous to the spreading of a liquid over a solid surface if the interfacial tension is low; and is only complicated because the surface of the supporting liquid is not an immobile plane as in the case of a solid.

*Failure of the Simple Theory.*—The fact that Coghill and Anderson's values of the angles did not agree with the simple theory, despite the fact that they were calculated on equations which should have secured agreement, indicated the need for a closer analysis of the lens equilibrium.

It is well known that the determination of surface tensions by Quincke's method (*loc. cit.*), based on the measurement of drops of liquid resting on a solid, gives values which are at least 10% too high. It was shown by Worthington (*Phil. Mag.*, 1885, 20, 51) that this is due to the neglect of the internal pressures caused by the curvature of the drop surfaces. Coghill and Anderson's equations must therefore involve errors of a similar magnitude.

The lenses used in this investigation were considerably smaller than those used by the earlier workers, and therefore this effect should be present in even greater intensity. An analysis of the results obtained confirmed this deduction, for, when the vertical and horizontal components of the surface tensions\* were evaluated in accordance with equations (1) and (2), it was found that their sum often differed considerably from zero. This is shown in Table II, in which cols. 4 and 8 should be zero if the equations were valid.

This effect of the internal pressure may be compared with the difference in the angle of contact between advancing, stationary, and retreating boundaries of a liquid on the surface of a solid. Nevertheless, there can be no direct comparison of the angles of a floating lens with the solid-liquid angles of contact, because the surface of the supporting liquid does not remain a plane.

\* The values of the surface tensions and interfacial tensions were chiefly taken from the International Critical Tables, Vol. 4. Those for the interfacial tensions between oleic acid and aqueous solutions of various  $p_H$  were Hartridge and Peters's values (*Proc. Roy. Soc.*, 1922, A, 101, 348), confirmed by the capillary-rise method with the actual solutions used in this investigation.

TABLE II.

Liquid.	Lens.	1.	2.	3.	4.	5.	6.	7.	8.
		$\sigma_{12}$ $\sin \alpha.$	$-\sigma_{23}$ $\sin \beta.$	$\sigma_{13}$ $\sin \gamma.$	$\Sigma \sigma$ $\sin \theta.$	$\sigma_{12}$ $\cos \alpha.$	$\sigma_{23}$ $\cos \beta.$	$-\sigma_{13}$ $\cos \gamma.$	$\Sigma \sigma$ $\cos \theta.$
Water	Oleic acid	5.6	-5.3	0.0	0.3	32.0	14.7	-42.5	4.2
HCl, $p_H$ 1.8	"	7.3	-7.5	1.5	1.4	31.7	14.1	-44.4	1.4
* $p_H$ 5.9	"	7.3	-9.8	0.0	-2.5	31.7	6.4	-41.0	-2.9
* $p_H$ 6.9	"	4.0	-9.6	0.0	-5.6	32.2	-1.0	-35.0	-3.8
C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	Water	40.8	-35.9	2.7	7.6	60.5	-5.7	-37.8	17.0
CCl <sub>4</sub>	"	34.3	-44.4	-5.0	-15.1	64.4	-7.0	-26.2	31.2
Paraffin	"	21.5	-40.7	3.1	-16.4	60.8	-30.7	-21.8	17.3
Water	C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	13.9	-27.1	11.4	-1.8	36.1	33.1	-72.5	-3.3
			to	to	to		to	to	to
			-15.4	7.6	6.1		24.4	-72.1	-11.6
"	Paraffin	9.3	-12.3	1.5	-0.5	19.9	49.5	-72.9	-3.5

\* These solutions were obtained by the use of phosphate buffers.

Neither of these series of angles can as yet be correlated with the known orientation of the molecules at the interface, nor can the molecular mechanism which decides the values of the angles of contact be determined. But the significance of the angle  $\gamma$  is quite clear, for it depends solely on the depth to which the lens is submerged. The vertical component of the surface tension of the lower liquid must support the lens if its weight and buoyancy do not exactly balance, and this component can only be zero (*i.e.*,  $\gamma = 0$ ) when these two forces are equal and opposite.

If  $W_1$  is the weight of the lens,  $W_2$  that of the lower liquid displaced, and  $r$  the radius of the lens, then

$$2\pi r \sigma_{13} \sin \gamma = W_1 - W_2 \quad \dots \quad (3)$$

if the small correction for the lowering of the meniscus of the lower liquid at the edge of the lens be neglected.

From Table III it is seen that this equation holds for all the lenses studied in this investigation: cols. 4 and 5 should be identical if the equation is valid, and the differences actually obtained are within the limits of experimental error. The weights were calculated from the cross sections of the lenses measured on the photographic plates, their areas and centres of gravity being determined directly. Weights are given in dynes and  $r$  in mm.

TABLE III.

Liquid.	Lens.	1.	2.	3.	4.	5.
		$r.$	$W_1.$	$W_2.$	$W_1 - W_2.$	$2\pi r \sigma_{13} \sin \gamma.$
Water	Oleic acid	1.6	1.36	0.96	0.4	0.0
$p_H$ 1.8	"	2.3	7.6	6.1	1.5	2.1
$p_H$ 5.9	"	1.95	9.2	8.8	0.4	0.0
$p_H$ 6.9	"	1.4	5.3	5.7	-0.4	0.0
$p_H$ 6.9	"	1.7	12.0	12.9	-0.9	0.0
C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	Water	1.46	5.25	4.1	1.15	2.4
CCl <sub>4</sub>	"	1.65	12.8	17.2	-4.4	-5.2
Paraffin	"	0.73	8.7	6.4	2.3	1.4
Water	Paraffin	1.77	2.5	1.4	1.1	2.4
"	C <sub>2</sub> H <sub>4</sub> Br <sub>2</sub>	1.89	17.8	5.5	12.3	13.3
"	"	1.89	11.1	2.5	8.6	9.0



In order to obtain a more definite analysis of the conditions of lens equilibrium, it is necessary to make assumptions which simplify the problem. The lenses which have been studied were not very large, and as their surfaces did not depart very much from segments of spheres, it is justifiable to assume that they actually had this shape. Under these conditions, the principle of virtual work may be used to make a more definite examination of the statical equilibrium of the lens.

Consider a lens of radius  $R$ , formed of two spherical segments of radii  $r_1$  and  $r_2$ , and heights  $h_1$  and  $h_2$  (Fig. 3). Then

$$R^2 = r_1^2 - (r_1 - h_1)^2 = 2r_1h_1 - h_1^2 = 2r_2h_2 - h_2^2 \quad (4)$$

Let the lens be given a small displacement increasing its radius to  $R + dR$  without transference of liquid from one segment to the other, *i.e.*, without altering the volume of either segment. Then  $R \cdot \Delta R = r \cdot \Delta h + h \cdot \Delta r - h \cdot \Delta h$ . The volume  $V$  of a segment of height  $h$  of a sphere of radius  $r$  is equal to  $\pi h^2(r - \frac{1}{3}h)$ , and therefore

$$\Delta V = \pi(2hr \cdot \Delta h + h^2 \cdot \Delta r - h^2 \cdot \Delta h)$$

By the conditions of the displacement,  $\Delta V = 0$ , hence  $\Delta r = -(2r - h)\Delta h/h$ , and by substitution in the above equation it follows that

$$R \cdot \Delta R = -r \cdot \Delta h = r \cdot \Delta A / 2\pi(r - h) \quad (5)$$

where  $A$  is the superficial area of the segment and is equal to  $2\pi rh$ . During this displacement work is done (1) by the surface tension forces, owing to change in superficial area of each surface of the lens and of the underlying liquid, (2) by the internal-pressure forces caused by the curvature of the lens surfaces, and (3) by gravity and the upward thrust of the displaced liquid, owing to the change in position of the centre of gravity of each segment of the lens. The magnitude and sign of these effects are now evaluated in turn, and the conditions of equilibrium are then obtained by equating their algebraic sum to zero.

(1) The total work done by the surface-tension forces is given by the algebraic sum of the products of the surface tensions and the change in area, *i.e.*, by

$$\sigma_{12}\Delta A_1 + \sigma_{23}\Delta A_2 - \sigma_{13}\Delta(\pi R^2) \cos \gamma$$

By substituting from (5), it is found that this work is equal to

$$2\pi R \cdot \Delta R[\sigma_{12}(1 - h_1/r_1) + \sigma_{23}(1 - h_2/r_2) - \sigma_{13} \cos \gamma] = 2\pi R \cdot \Delta R[\sigma_{12} \cos \alpha + \sigma_{23} \cos \beta - \sigma_{13} \cos \gamma] \quad (6)$$

Neumann's triangle [equation (2)] demands that the expression between the brackets should be zero for equilibrium. This follows necessarily where only the surface tensions are considered.

(2) Under the conditions governing the displacement given to the lens (*i.e.*, no volume change of either segment), the total work done by the internal pressures is found to be zero if the lens surfaces are accurately spherical segments, thus: The displacement of a ring of the surface subtending an angle  $\omega$  at the centre of curvature is  $\Delta r \cdot (1 - \cos \omega) + \Delta h \cdot \cos \omega$ ; the total work done by the internal pressure is therefore

$$\int \frac{2\sigma}{r} \cdot 2\pi r^2 \Delta(\cos \theta) [\Delta r \cdot (1 - \cos \omega) + \Delta h \cdot \cos \omega] \quad (7)$$

and on integration and substitution this integral is found to vanish.

(3) The height of the centre of gravity of a spherical segment above its basal plane is

$$\bar{h}_1 = R^4/4h^2(r - \frac{1}{3}h) - (r - h) \quad (8)$$

The work done by gravity on the lens is  $-gV_1\rho_1 \cdot \Delta h_1$ , and the work done by the upward thrust is therefore  $-gV_2(\rho_2 - \rho_1) \cdot \Delta h_2$ , where  $V_1$  and  $V_2$  are the volumes of the upper and lower segments of the lens, and  $\rho_1$  and  $\rho_2$  are the densities of the lens liquid and the supporting liquid, respectively.

By differentiating equation (8) and substituting from equations (4) and (5), it follows that the total work from both these causes is equal to

$$-2\pi R \cdot \Delta R \cdot g \cdot [\frac{1}{2}R^2\rho_2 - h_1\rho_1(r_1 - \frac{1}{3}h_1) - h_2(\rho_2 - \rho_1)(r_2 - \frac{1}{3}h_2)] \quad (9)$$

Now, from the principle of virtual work, the sum of expressions (6) and (9) must be zero; the conditions for equilibrium are therefore given by

$$[\sigma_{12} \cos \alpha + \sigma_{23} \cos \beta - \sigma_{13} \cos \gamma] - g[\frac{1}{2}R^2\rho_2 - h_1\rho_1(r_1 - \frac{1}{3}h_1) - h_2(\rho_2 - \rho_1)(r_2 - \frac{1}{3}h_2)] = 0 \quad (10)$$

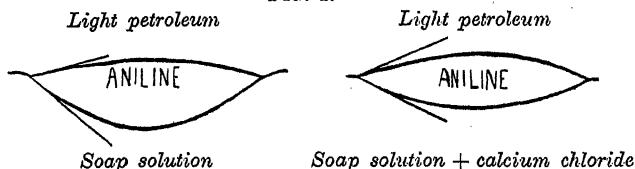
This equation may be tested experimentally. All the relevant data are obtained from the photographic plates, and collected in Table IV (linear measurements being in mm., and tensions in dynes/cm.). Col. 6 reproduces the values of the first term in equation (10) as given in Table II (col. 8) for the examination of equation (2); col. 7 contains the (negative) values of the second term in equation (10) which is applied as a correction to equation (2). The smallness of the algebraic sum of cols. 6 and 7, as given in col. 8, shows that the agreement between equation (10) and experiment is good, and that this equation is a definite improvement on the simpler equation (2) derived from Neumann's triangle. Lenses of carbon tetrachloride, ethylene dibromide, and paraffin on water still show a serious discrepancy. In these cases, the photographic records indicated that the segments were markedly divergent from spheres

TABLE IV.

Liquid.	Lens.	1. R.	2. $h_1$ .	3. $r_1$ .	4. $h_2$ .	5. $r_2$ .	6. $\Sigma \cos \theta$ .	7.	8.
Water	Oleic acid	1.6	0.16	7.7	0.20	4.15	4.2	-1.3	2.9
$p_H$ 1.8	"	2.3	0.32	8.1	0.60	5.36	1.4	-0.8	0.6
$p_H$ 5.9	"	1.95	0.24	8.7	1.07	2.50	-2.9	2.4	-0.5
$p_H$ 6.9	"	1.40	0.10	14.1	1.37	1.54	-3.8	3.9	0.1
$p_H$ 6.9	"	1.7	0.10	12.1	1.83	2.1	-3.8	3.5	-0.3
$p_H$ 9.7	"	1.7	0.0	—	1.6	1.6	-0.5	-1.5	-2.0
							(app.)		(app.)
Water	Paraffin	1.77	0.40	4.75	0.28	8.3	-3.5	3.7	0.2
"	$C_2H_5Br_2$	1.89	0.41	6.8	0.49	4.76	-3.3	2.0	-1.3
"	"	1.89	0.41	6.8	1.11	1.7	-11.6	8.0	-3.6
$C_2H_5Br_2$	Water	1.46	0.47	2.60	0.85	1.9	17.0	-1.8	15.2
$CCl_4$	"	1.65	0.46	2.80	1.71	1.6	31.2	1.0	32.2
Paraffin	"	0.73	0.09	25.0	2.44	1.3	17.3	-2.2	15.1

(the lenses of oleic acid on very alkaline solutions were also not spherical), and the discrepancy between theory and experiment must be attributed to this fact. When the lens surfaces approach segments of spheres satisfactory agreement is obtained. It is seen that Neumann's triangle is obeyed only for very large drops, in which forces other than the surface tensions are negligible.

FIG. 4.



*Floating Lenses at the Liquid-Liquid Interface.*—When water was placed at a light petroleum-aniline interface, it spread completely over it, but when the surface tension of the water was lowered by the dissolution of a small quantity of soap (0.01% of sodium palmitate) a floating lens was obtained of which the angles were  $\alpha = 30^\circ$ ,  $\beta = 76^\circ$ ,  $\gamma = 0^\circ$ . Lenses of aniline were similarly formed at the light petroleum-soap solution interface, the angles being  $\alpha = 14^\circ$ ,  $\beta = 52^\circ$ ,  $\gamma = 14^\circ$ .

It was thought the addition of calcium chloride to the soap solution might prove interesting from the point of view of the theory of emulsions. Actually, such addition did alter the angles of the lens, and when sufficient calcium chloride was added to carry the solution over the inversion point, the angles became  $\alpha = 25^\circ$ ,  $\beta = 24^\circ$ ,  $\gamma = 0^\circ$ , for a lens of aniline between light petroleum and the aqueous solution, and  $\alpha = 25^\circ$ ,  $\beta = 95^\circ$ ,  $\gamma = 35^\circ$ , when the aqueous solution was floating between the other liquids. The former case is the more interesting, for here it was clearly seen that the alteration of the lens shape was illustrative of the phenomenon of emulsion inversion (compare Fig. 4), the curvature of the lower surface being greatly diminished owing to the tendency to curve in the opposite direction.

When these observations were compared with those on oleic acid, where a large curvature was associated with a low interfacial tension, it was seen that this tendency towards inversion could be explained by the raising of the interfacial tension  $\sigma_{23}$ .

Bancroft and Tucker (*J. Physical Chem.*, 1927, **31**, 1681) have deduced that the character of an emulsion is determined by the sign of the difference  $\sigma_{23} - \sigma_{12}$ . If  $\sigma_{23} > \sigma_{12}$  the water will tend to be emulsified in the oil, but if  $\sigma_{23} < \sigma_{12}$  the oil will tend to be emulsified in the water. The present observations support these conclusions by direct experiment, since it is concluded that the raising of the interfacial tension  $\sigma_{23}$  is favourable to inversion from oil in water to water in oil.

The changes occurring when the soap solution lies between the aniline and the light petroleum were neither as large nor as definite as in the case just considered. This may now be attributed to the fact that  $\sigma_{23}$  and  $\sigma_{12}$  were affected in roughly the same proportion.

*The Mechanism of Emulsification by Soap.*—Practically all the theories advanced to explain emulsification have received much adverse criticism, and Bancroft and Tucker believe that the surface-tension relationship mentioned above affords the only criterion by which the character of the emulsion can be decided. An objection to this view is that it gives no clue to the molecular mechanism of emulsification.

An attempt has been made to elucidate the mechanism in the case of emulsification by soap. The explanation tentatively suggested is based on the results of experiments on film dissolution (Lyons and Rideal, *Proc. Roy. Soc.*, 1929, *A*, **124**, 343), and on a modification of the wedge theory of emulsions. This theory in its original form broke down when it was shown that the molecules in the interfacial film were by no means close-packed, for Griffin (*J. Amer. Chem. Soc.*, 1923, **45**, 1648) found that the area occupied by a soap molecule at the oil-water interface was 44 Å.U., whereas Harkins and Beeman (*ibid.*, 1929, **51**, 1674) showed that an emulsion could be formed with an interfacial area of 190 Å.U.

The film experiments proved that a residual bimolecular film of acid soap was the stable surface configuration on alkaline solutions. It was thought that such a bimolecular leaflet might also be present at the oil-water interface, in which case it would have a profound influence on the emulsifying power of the soap solution.

There was little evidence by which the probability of this assumption could be judged,\* but Briggs and Schmidt (*J. Physical Chem.*,

\* Miss Laing (*Proc. Roy. Soc.*, 1925, *A*, **109**, 28) had concluded that the existence of the bimolecular leaflet was proved by Griffin's results, but her conclusions were based on a misunderstanding.

1925, 19, 479) had noticed that the stability of an emulsion of benzene in soap solution was increased by the addition of 0.1% of free alkali, although further alkali decreased the stability. It seemed possible that this variation in the stability of the emulsions might be connected with the alteration in composition of the residual bimolecular film with change in the alkalinity of the solutions, and experiments were therefore devised to test this possibility. A series of soap solutions of known  $p_H$  was made by the addition of caustic soda to a 0.01% sodium palmitate solution. A preliminary electrometric titration had been carried out to ensure that the solutions were made of standard alkalinity. These solutions were shaken with benzene under standardised conditions, and the stabilities of the emulsions thus formed were compared. Although the experiments were only semi-quantitative, the results obtained were quite definite.

On solutions more acid than  $p_H$  8.0, both the benzene-in-water and the water-in-benzene emulsion had but little stability, but that of the former phase steadily increased from  $p_H$  8.0 to  $p_H$  10.0 at which it reached a maximum. The latter emulsion only attained an appreciable stability on solutions more alkaline than  $p_H$  10.0, and stability increased with alkalinity until salting-out of the soap occurred. Both phases were almost equally stable in the  $p_H$  range 10—12. It was also observed that the frothing power of a soap solution ran strictly parallel to the stability of the benzene-in-water phase, and also reached a maximum at  $p_H$  10.0.

The existence of the bimolecular leaflet at the surface of soap solutions seems well-established, and the similarity between frothing power and emulsifying power seemed to confirm the presence of this bimolecular leaflet at the benzene-water interface. A comparison was therefore made between the  $p_H$  values obtained in these emulsion experiments and in the film experiments, and it was found that they were identical.

On solutions where a benzene-in-water emulsion is the more stable, the film experiments showed that the lower layer of the equilibrium bimolecular leaflet was not completely packed. On very alkaline solutions, where a water-in-benzene emulsion is the more stable, the equilibrium bimolecular film had considerably less than half the area of the original unimolecular film. On solutions where the two layers were equally packed, the emulsions were of almost equal stability. These observations, therefore, support the view that emulsification depends on the presence of a bimolecular leaflet, while a unimolecular film shows little tendency to cause emulsion formation.

The mechanism of emulsification may now be pictured as follows.

When a soap molecule is first adsorbed at the interface it will be in the form  $\text{NaP,HP}$ , and will thus give a double film equally packed on either side. On solutions less alkaline than  $p_H 10$  the equilibrium lower (aqueous) layer will be less densely packed than the upper layer, and this equilibrium state must be reached by one of two processes, *viz.*, either a transference of molecules across the interface, or a curving of the boundary. In emulsion formation the latter effect predominates. In order to increase the packing of the upper layer and decrease that of the lower layer of the initially symmetrical film, the boundary curves with the upper layer inside, squeezing it and giving an oil-in-water emulsion. A similar analysis accounts for the stability of water-in-oil emulsions on very alkaline solutions where the lower layer is probably more closely packed than the upper. Over the range at which a symmetrical leaflet is stable, the boundary will not curve preferentially in either direction, and neither form of emulsion will be more stable than the other.

These experiments have shown that this tentative suggestion of the bimolecular leaflet at the oil-water interface is consistent with the known data on emulsification by soaps. There is not yet sufficient evidence to show whether a similar explanation can be applied to other cases.

#### *Summary.*

The shapes and angles of liquid lenses floating on the surface of a different liquid have been studied by a photomicrographic method. The angles are subject to wide variations, and are especially sensitive to alterations in the interfacial tension between the two liquids. It has been shown, further, that these angles differ from those calculated on the basis of Neumann's triangle, and the causes of the difference have been investigated.

The contact angles at a junction of three liquids have been investigated with reference to the theory of emulsification. It has been suggested that emulsification by soap may be determined by the existence of a bimolecular soap leaflet at the oil-water interface.

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LXXXIV.—*The Determination of the Dissociation Pressures of Hydrated Salts by a Dynamical Method. Part III.*

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A FULL account of previous work on the subject of dissociation pressures of salt hydrates is given in Parts I and II of this series (Partington, J., 1911, 99, 467; Partington and Huntingford, J., 1923, 123, 160) and by Menzies (*J. Amer. Chem. Soc.*, 1920, 42, 978, 1952).

Since the publication of Part II, two papers have appeared in which a method similar to that described has been employed (Schumb, *J. Amer. Chem. Soc.*, 1923, 45, 342; Baxter and Cooper, *ibid.*, 1924, 46, 923. These workers used a method almost identical with that used by Baxter and Lansing, *ibid.*, 1920, 42, 419, entailing the measurement of the volume of air aspirated over the salt).

In this research the original method of Parts I and II has been employed, which is essentially as follows. Air, dried over calcium chloride and phosphoric oxide, is passed successively over the salt, through phosphoric oxide tubes, through a water bubbler, and finally through a further apparatus for absorbing water vapour. Since the salt and the water are both maintained at the same temperature, the weights of water absorbed in the respective series of tubes are, apart from small corrections applied, directly proportional to the vapour pressures of the salt and of the water.

*Apparatus.*—The U-tube containing the salt was 2 cm. in internal diameter and the total length of the column of salt was 50 cm. It was connected with a trap to condense part of the water vapour before the moist air reached the absorption tubes (see Part I). The water bubbler had a similar trap fitted. This part of the apparatus was immersed in an electrically controlled thermostat, steady to within  $\pm 0.01^\circ$ .

The absorption apparatus consisted of two U-tubes fitted with glass stoppers and filled with phosphoric oxide and glass wool. Only the first tube was weighed, the other acting as a guard tube between the absorption tube proper and the water bubbler or the aspirator. The traps and corresponding absorption tubes were weighed together.

Air was drawn through this apparatus by an aspirator bottle of 10 litres capacity, out of which water was siphoned. This bottle was fitted with a mercury manometer to indicate the difference in pressure between the atmosphere and the inside of the bottle.

Before passing through the apparatus, the air was dried and freed from carbon dioxide by passage through (i) a sulphuric acid bubbler which also served to indicate the rate of flow, (ii) a series of caustic soda tubes, (iii) a calcium chloride tube, and finally (iv) a phosphoric oxide tube, since this reagent was used in the absorption tubes.

When in use the ground joints were cemented outside with Faraday wax, with the exception of the joints in the traps, which were lubricated with petroleum jelly. Both the wax and the jelly were removed by cotton wool and benzene before the respective parts were weighed. The traps and tubes were weighed against counterpoises of similar structure.

*Materials.*—(1) *Disodium hydrogen phosphate dodecahydrate*,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . A.R. Salt from B.D.H. was used after one recrystallisation. A small amount of the heptahydrate was prepared by crystallising the salt above  $36^\circ$ , the transition point between these two hydrates being at  $35.4^\circ$  (D'Ans and Schreiner, *Z. physikal. Chem.*, 1911, **75**, 99). An intimate mixture of the two powdered hydrates was used. This overcame the necessity of passing air through the salt for a considerable time before the actual determinations were commenced, as had been done previously, since the two phases were present from the start.

(2) *Disodium hydrogen arsenate hydrates*. In Part II, dissociation pressures of sodium arsenate dodecahydrate were determined at  $25^\circ$ ,  $30^\circ$ , and  $35^\circ$ . It was pointed out that the result at  $25^\circ$ , viz., 11.10 mm., did not agree with that obtained by Lescœur (*Compt. rend.* 1887, **164**, 1171; *Ann. Chim. Phys.*, 1890, **21**, 556), viz., 9.8 mm. at that temperature. At  $30^\circ$  the difference was only 0.25 mm. Lescœur had, however, indicated a transition point at  $23^\circ$  between two hydrates to which he assigned the formulæ " $2\text{NaO}, \text{AsO}^5, 25\text{HO}$ " and " $2\text{NaO}, \text{AsO}^5, 15\text{HO}$ ," which correspond with the dodeca- and hepta-hydrates  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$  and  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ . Confirmation of this transition was obtained by Rosenheim and Thon (*Z. anorg. Chem.*, 1927, **167**, 7), who found that the solubility curve for sodium arsenate in water shows a marked transition at  $22^\circ$  between these two hydrates. It was clear, therefore, that the determinations above  $20^\circ$  were in need of revision.

Tilden (J., 1884, **45**, 269) gives the m. p. of sodium arsenate dodecahydrate as  $28^\circ$ , but if this were correct the results in Part II could not have been obtained, since the apparatus employed would have become choked with the fused salt. Lescœur says that the salt partially melts at  $23^\circ$ . Actually, at  $22^\circ$ , we found that the salt becomes only damp, and this increases with temperature until the salt finally becomes completely liquid; this liquid becomes clear at



56.2°, and is then a true solution of the heptahydrate. The liquid, when supercooled to, say, 40° and seeded with a crystal of salt, deposits crystals of the heptahydrate and the temperature rises to 56.2°. There is a similar evolution of heat at 22°, but this is not so well marked. The original tube used in Part II was available and it showed that the salt used had not undergone fusion.

It was hoped that the dissociation-pressure curves would also show the transition point at 22° with some accuracy, but it became clear that the solubility curve (Rosenheim and Thon, *loc. cit.*) provided a more accurate result, as the angle between the dissociation-pressure curves is small. We have therefore, in calculating the heats of hydration and plotting the curves, assumed that the latter actually cut at 22°, an assumption which was made very probable by the actual results.

The dodecahydrate was prepared by crystallising the salt below 22°; it is efflorescent at room temperature in air. The heptahydrate was similarly prepared by crystallisation above 22°, *viz.*, at about 30°; this hydrate does not effloresce appreciably at room temperature in air. The anhydrous salt was obtained by heating the crystalline salt at 120° until it lost its water of crystallisation. The appropriate pairs of phases were then intimately mixed and used in the U-tubes as indicated above.

### Results.

The method of working out the results is the same as that used in Part II of this series. The equation derived,\* with which the results are calculated, is

$$p = \frac{p'KB}{B + p'K} = \frac{\frac{w_1}{w_2} \pi \cdot \left( \frac{B-b}{B-b-\pi} \right) B}{B + \frac{w_1}{w_2} \pi \cdot \left( \frac{B-b}{B-b-\pi} \right)} \quad (1)$$

where  $p$  is the dissociation pressure of the salt at  $t^\circ$ ;  $w_1$  and  $w_2$  are the weights (in grams) of water vapour absorbed from the salt and the water, respectively;  $\pi$  is the vapour pressure of water at  $t^\circ$ ;  $B$  is the barometric height; and  $b$  is the difference of levels in the gauge fitted to the aspirator. All pressures are given in mm. of mercury.

This method corrects for: (a) the pressure difference between the air in the bottle and the atmosphere; (b) the head of water in the bubbler; (c) the larger volume of the moist air in equilibrium with the water as compared with that in equilibrium with the salt.

\* The formula given on p. 167 of Part II was incorrectly reproduced, but all the results given in that paper were in fact calculated by the correct formula as now given.

*Sodium arsenate dodecahydrate in presence of heptahydrate.*Temp. 14·90°;  $\pi = 12\cdot706$  mm.

$w_1$ .	$w_2$ .	B.	b.	p.
0·0162	0·0403	762·5	22	5·16
0·0202	0·0491	757·0	22·5	5·27
0·0172	0·0430	756·9	22	5·13
0·0186	0·0442	753·8	22·5	5·38
0·0193	0·0468	761·5	20	5·29
0·0174	0·0431	766·2	19·5	5·17
0·0178	0·0439	753·6	22	5·20
0·0178	0·0439	757·3	22	5·29

Mean result:  $p_{14\cdot90^\circ} = 5\cdot24$  mm.Temp. 20°;  $\pi = 17\cdot535$  mm.

$w_1$ .	$w_2$ .	B.	b.	p.
0·0236	0·0562	761·2	21	7·47
0·0197	0·0482	769·06	20·5	7·27
0·0179	0·0417	774·3	19·5	7·42
0·0228	0·0544	759·5	20	7·25
0·0198	0·0478	756·2	20	7·23
0·0179	0·0430	772·7	18·5	7·41
0·0209	0·0488	760·05	18·5	7·50

Mean result:  $p_{20^\circ} = 7\cdot36$  mm.*Sodium arsenate heptahydrate in presence of anhydrous salt.*Temp. 24·92°;  $\pi = 23\cdot658$  mm.

0·0499	0·1197	762·87	18·5	9·95	0·0417	0·1002	762·9	19·7	10·07
0·0454	0·1019	769·6	19	10·11	0·0433	0·1013	766·9	20	10·20
0·0430	0·1029	765·6	19·5	10·11	0·0435	0·1039	780·9	19	10·12
0·0408	0·0972	763·4	19	10·16	0·0463	0·1054	781·7	20	10·14
0·0423	0·1047	770·3	19	9·80	0·0430	0·1013	764·6	19·4	10·28
0·0468	0·1057	772·7	20	10·17	0·0464	0·1131	766·5	19·7	9·93
0·0423	0·1043	775·0	21	9·82	0·0501	0·1193	764·15	18·5	9·73
0·0444	0·1088	773·4	21·5	9·86					

Mean result:  $p_{24\cdot92^\circ} = 9\cdot98$  mm.Temp. 30°;  $\pi = 31\cdot824$  mm.

0·0417	0·0939	766·9	23	14·48
0·0443	0·0993	763·0	25	14·55
0·0486	0·1109	762·0	26·5	14·30
0·0439	0·1010	758·3	25·6	14·20
0·0489	0·1112	768·7	25	14·34
0·0389	0·0870	761·2	25	14·60
0·0428	0·0958	759·0	24·2	14·60

Mean result:  $p_{30^\circ} = 14\cdot39$  mm.Temp. 35°;  $\pi = 42\cdot175$  mm.

0·0684	0·1434	767·1	22	20·75
0·0639	0·1341	763·0	22	20·73
0·0603	0·1275	757·2	22	20·56
0·0723	0·1515	758·0	21	20·75
0·0717	0·1509	749·3	22·5	20·67
0·0619	0·1296	760·0	19	20·78
0·0601	0·1254	757·7	22	20·84
0·0597	0·1250	753·2	23	20·77

Mean result:  $p_{35^\circ} = 20\cdot73$  mm.*Sodium phosphate dodecahydrate in presence of heptahydrate.*Temp. 14·90°;  $\pi = 12\cdot706$  mm.

0·0358	0·0513	751·0	22	8·91
0·0328	0·0468	757·7	20	8·95
0·0354	0·0507	758·1	19·5	8·92
0·0368	0·0529	759·0	22	8·87
0·0401	0·0569	762·5	21	9·01
0·0372	0·0534	768·2	22·5	8·90
0·0385	0·0549	760·0	22·5	8·96

Mean result:  $p_{14\cdot90^\circ} = 8\cdot93$  mm.Temp. 20°;  $\pi = 17\cdot535$  mm.

0·0472	0·0661	748·3	22	12·91
0·0503	0·0703	752·4	22	12·94
0·0487	0·0681	757·3	21	12·91
0·0453	0·0637	755·7	20·5	12·90
0·0496	0·0691	762·0	22	12·95
0·0521	0·0727	763·1	22·5	12·95
0·0453	0·0633	764·3	22	12·94

Mean result:  $p_{20^\circ} = 12\cdot93$  mm.Temp. 24·92°;  $\pi = 23\cdot658$  mm.

0·0755	0·0933	768·3	16	19·27
0·0678	0·0838	773·6	15·5	19·14
0·0710	0·0884	764·6	16	19·01
0·0650	0·0818	764·5	16	18·97
0·0696	0·0855	762·05	18	19·14
0·0707	0·0874	761·9	17	19·27
0·0602	0·0745	760·6	17	19·27
0·0571	0·0710	759·3	16	19·18
0·0698	0·0864	756·9	16	19·27
0·0605	0·0759	748·06	19·5	19·01
0·0714	0·0890	755·12	19·1	19·14

Mean result:  $p_{24\cdot92^\circ} = 19\cdot10$  mm.Temp. 30°;  $\pi = 31\cdot824$  mm.

0·0905	0·1064	767·06	23	27·29
0·0815	0·0974	769·6	22	26·86
0·0786	0·0915	768·8	21	27·47
0·0695	0·0836	769·3	21	26·66
0·0695	0·0828	768·6	21	26·92
0·0801	0·0934	755·4	20·5	27·48
0·0724	0·0870	753·1	21	26·71

Mean result:  $p_{30^\circ} = 27\cdot05$  mm.

## Discussion.

The foregoing results are collected in Table I, and Fig. 1 shows the curves obtained by plotting  $p$  against  $t$  and also  $\log p$  against  $1/T$  (where  $T = t + 273^\circ$ ). The logarithmic plots are straight

FIG. 1.

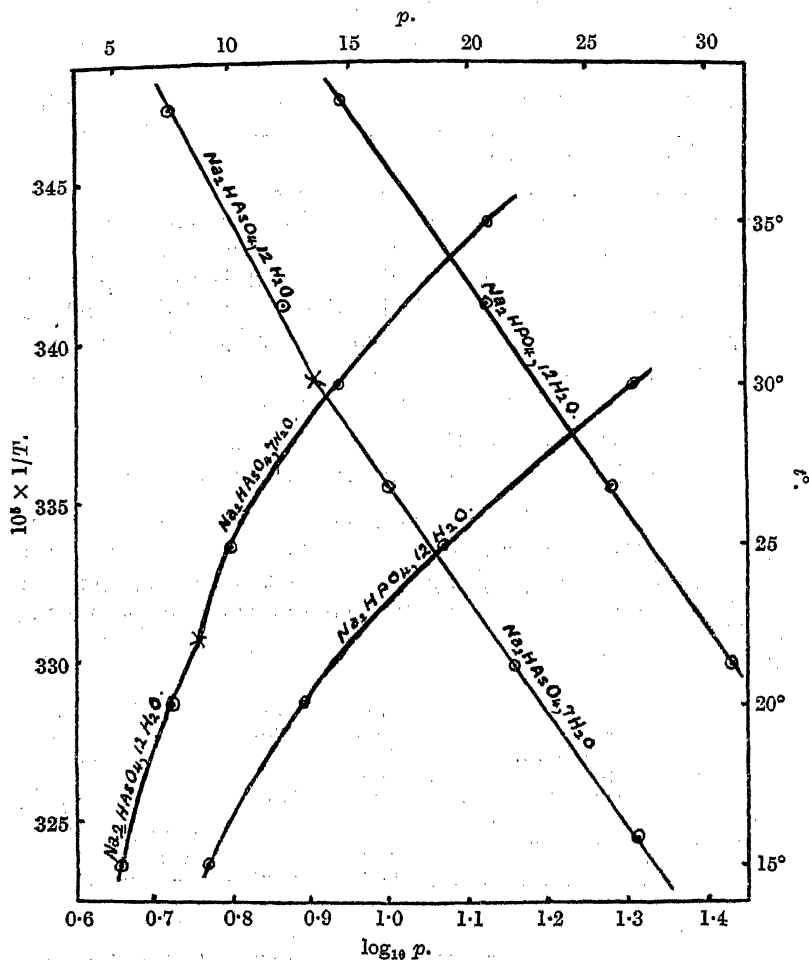


TABLE I.

Hydrates.	$p_{14-20^\circ}$ , mm.	$p_{20^\circ}$ , mm.	$p_{24-22^\circ}$ , mm.	$p_{30^\circ}$ , mm.	$p_{35^\circ}$ , mm.
$\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O} \rightarrow 7\text{H}_2\text{O}$	5.24	7.36	—	—	—
$\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O} \rightarrow 0\text{H}_2\text{O}$	—	—	9.98	14.39	20.73
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \rightarrow 7\text{H}_2\text{O}$	8.93	12.93	19.10	27.05	—

lines, and in the case of sodium arsenate there is a definite intersection of the lines for the two hydrates. It has been pointed out, however, that this is not a very accurate method of finding the transition point.

For comparison with those of other authors, the present results were plotted and the values for 15° and 20° interpolated. Where possible, results for 15°, 20°, 25°, and 30° were found by a similar process from results of previous workers. In the case of Lescœur's results for sodium arsenate this was not possible, as the points did not lie on a regular curve. The same was found to be the case with the results of Müller Erzbach (*Ber.*, 1887, 20, 137; *Z. physikal. Chem.*, 1896, 19, 134) above 20°.

*Sodium arsenate.* Lescœur gives, for this salt, three series of vapour pressures, one for each of the two hydrates, and one for the saturated solution. His results for the dodecahydrate and the solution led to comparatively smooth curves and the vapour pressure is given for both as 16 mm. at 20°; but those for the dodeca- and the hepta-hydrate do not agree with ours, being: at 15°, 11.5 mm. and 3.4 mm. respectively, and at 20°, 16 mm. and 4.6 mm. respectively. The only comparable results are:

At 25°: This research 10 mm.; Lescœur 9.8 mm.

At 30°: This research 14.39 mm.; Lescœur 15 mm.

*Sodium phosphate.* The results given by Lescœur (*Ann. Chim. Phys.*, 1890, 21, 548) for this salt are identical in every way with those given by Debray (*Compt. rend.*, 1868, 66, 194). Table II compares the results of several previous workers with the present results.

TABLE II.

Author.	$P_{15^{\circ}}$ , mm.	$P_{20^{\circ}}$ , mm.	$P_{25^{\circ}}$ , mm.	$P_{30^{\circ}}$ , mm.
Debray * (interpolated) .....	9.0	13.0	18.2	27.1
Müller Erzbach † (interpolated) .....	9.0	13.5		
Frowein ‡ (interpolated) .....	8.84	12.6	18.5	28
Foote and Scholes § .....			18	
Wilson    .....			19.13	
Baxter and Cooper ¶ .....	8.93		19.05	
This research .....	8.95	12.93	19.18	27.05

\* *Loc. cit.*

† *Loc. cit.*

‡ *Z. physikal. Chem.*, 1887, 1, 362; "Revue de Chimie physique d'Ostwald et van 't Hoff," t. ii, p. 362.

§ *J. Amer. Chem. Soc.*, 1911, 33, 1309.

|| *Ibid.*, 1921, 43, 704.

¶ *Ibid.*, 1924, 46, 923.

*Heats of Hydration.*—The heats of hydration were calculated from

the dissociation pressures by the Clapeyron-Clausius equation in the form

$$Q(\text{g.-cals.}) = 4.576 \frac{T_2 T_1}{T_2 - T_1} \log \left( \frac{p_2/\pi_2}{p_1/\pi_1} \right) \quad (2)$$

The values obtained are given in Table III. Those for sodium

TABLE III.

Reaction.	Temperature range.	Q per mol. H <sub>2</sub> O.	Q for whole reaction.
Na <sub>2</sub> HAsO <sub>4</sub> ·12H <sub>2</sub> O	14.90—20°	579	2,895
→ Na <sub>2</sub> HAsO <sub>4</sub> ·7H <sub>2</sub> O + 5H <sub>2</sub> O(liq.)	20 —22	589	2,949
Na <sub>2</sub> HAsO <sub>4</sub> ·7H <sub>2</sub> O	22 —24.92	2,847	19,929
→ Na <sub>2</sub> HAsO <sub>4</sub> + 7H <sub>2</sub> O(liq.)	24.92—30	3,065	21,455
	30 —35	3,092	21,644
Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	14.90—20	2,339	11,697
→ Na <sub>2</sub> HPO <sub>4</sub> ·7H <sub>2</sub> O + 5H <sub>2</sub> O(liq.)	20 —24.92	2,359	11,795
	24.92—30	2,396	11,978

phosphate may be compared with those of Baxter and Cooper (*loc. cit.*), Q being given in g.-cals. :

	Q <sub>15-20°</sub> .	Q <sub>20-25°</sub> .	Q <sub>25-30°</sub> .
Baxter and Cooper .....	11,340	12,180	—
Present work .....	11,697	11,795	11,978

The three series of heats of hydration show an increase with rise of temperature, as Baxter and Cooper also found for sodium phosphate, acetate, and carbonate. For the last two salts, however, directly determined values show the opposite effect.

In the case of sodium phosphate hydrates, data are available for the heats of solution at 18° and a dilution of 400 mols. of water per mol. of salt. For the dodecahydrate, Thomsen (*J. pr. Chem.*, 1878; 17, 174) gives —22,820 g.-cals., and Pfaundler (*Ber.*, 1871, 4, 775) —22,500 g.-cals. For the heptahydrate at the same dilution and temperature, Pfaundler (*loc. cit.*) gives —11,300 g.-cals. Pfaundler's values give the heat of the reaction



as 11,200 g.-cals. (*i.e.*, 2240 g.-cals. per mol. of water) at 18°, which is in satisfactory agreement with the results obtained from the dissociation pressures.

Another method available for the calculation of the heats of hydration of the salts is based on Nernst's heat theorem. This gives for the intrinsic energy change (here the quantity of heat liberated as found thermochemically) :

$$Q = Q_0 + \alpha T^2 + \beta T^3 \quad (3)$$

and for the free-energy change :

$$A_T = Q_0 - \alpha T^2 - \frac{\beta}{2} T^3 \quad (4)$$

$\alpha$  and  $\beta$  being the same constants in both equations. The values of  $A_T$  (in g.-cals.) may be found from the dissociation pressures by the equation

$$A_T = RT \log_e \pi/p \quad (5)$$

where  $p$  and  $\pi$  have the values assigned in equation (1) and  $R = 1.9875$ .

The most satisfactory method for calculating  $Q_0$  and  $\alpha$  ( $\beta$  being negligibly small) from the equations obtained by applying (4) to each experimental temperature is that of least squares. By substituting the values of  $Q_0$  and  $\alpha$  so obtained in equation (3) we obtain the values of  $Q$  for various temperatures. Table IV compares the results thus derived with those calculated by the Clapeyron-Clausius equation (2) as in Table IV: the former are somewhat lower than the latter.

TABLE IV.

Reaction.	Temp.	$Q_0$ per mol. H <sub>2</sub> O.	$\alpha \times 10^5$ .	$A_T$ , per mol. of H <sub>2</sub> O.	$Q$ , per mol. of H <sub>2</sub> O.	$Q$ for whole reaction, eq. (3).	$Q$ for whole reaction, eq. (2).
Na <sub>2</sub> HAsO <sub>4</sub> ·12H <sub>2</sub> O → Na <sub>2</sub> HAsO <sub>4</sub> ·7H <sub>2</sub> O + 5H <sub>2</sub> O(liq.)	14.90° 20	542.43	43.71	506.20 504.90	578.8 579.9	2,894 2,899	2,895
Na <sub>2</sub> HAsO <sub>4</sub> ·7H <sub>2</sub> O → Na <sub>2</sub> HAsO <sub>4</sub> + 7H <sub>2</sub> O(liq.)	24.92 30 35	1646.9	1278	510.40 477.36 434.21	2781.2 2820.3 2858.3	19,468 19,742 20,008	21,455 21,644
Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O → Na <sub>2</sub> HPO <sub>4</sub> ·7H <sub>2</sub> O + 5H <sub>2</sub> O(liq.)	14.90 20 24.92 30	1186.8	1180	196.95 177.17 153.77 97.76	2175.8 2209.6 2241.8 2280.1	10,879 11,048 11,209 11,400	11,697 11,795 11,978

For sodium phosphate dodecahydrate, by the method just employed, Müller (*J. Chim. physique*, 1909, 7, 534) found from Frowein's results (*loc. cit.*) that  $Q = 2215.3$  g.-cals. per mol. of water at 18° ( $Q_0 = 1200.58$ ;  $\alpha = 1198.27 \times 10^{-5}$ ).

To values of the specific heats of the dodeca- and hepta-hydrates of sodium phosphate as found by Nernst, Koref, and Lindemann (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1910, 12, 247), viz., between 34.4° and 1.9°, 0.3723 for the dodecahydrate, and 0.3230 for the heptahydrate, an equation of the type

$$dQ/dT = C_A + C_B - C_C = \alpha t. \quad (6)$$

has been applied, in which  $C_A$ ,  $C_B$ , and  $C_C$  are the molecular heats of the heptahydrate, of 5H<sub>2</sub>O(liq.), and of the dodecahydrate, respectively. Since the specific heats were determined over a wide range,  $t$  is not accurately defined but it was taken as 18°, this being approximately the mean of 34.4° and 1.9°;  $\alpha$  then becomes 0.1501, which is about ten times the value calculated previously.

There being no data concerning the specific heats of the hydrates of sodium arsenate, these were determined approximately over the

range  $+16^{\circ}$  to  $-12^{\circ}$ , the method of mixtures being used with carbon tetrachloride as the calorimetric liquid. The value 0.206 was taken as the specific heat of carbon tetrachloride at  $-12^{\circ}$  by interpolation from the results of Latimer (*J. Amer. Chem. Soc.*, 1922, 44, 90), Mills and MacRae (*J. Physical Chem.*, 1911, 15, 54), and Timofejew (*Iszv. Kiew polyt. Inst.*, 1905, 1).

The results so obtained were: Dodecahydrate, 0.414 g.-cal./g.; heptahydrate, 0.350 g.-cal./g., whence the respective molecular heats are 166.3 and 109.3 g.-cals. Then, from equation (6), for the reaction  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O} \longrightarrow \text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O} + 5\text{H}_2\text{O}(\text{liq.})$ ,  $\alpha = 0.1178$ , again about ten times that previously calculated.

### Summary.

The dissociation pressures of sodium arsenate hydrates have been redetermined, and some values for sodium phosphate hydrates are also given. The results obtained are:

For the reaction  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O} \longrightarrow \text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O} + 5\text{H}_2\text{O}$ , at  $14.90^{\circ}$ , 5.24 mm.; and at  $20^{\circ}$ , 7.36 mm.

For the reaction  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O} \longrightarrow \text{Na}_2\text{HAsO}_4 + 7\text{H}_2\text{O}$ , at  $24.92^{\circ}$ , 9.98 mm.; at  $30^{\circ}$ , 14.39 mm.; and at  $35^{\circ}$ , 20.73 mm.

For the reaction  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} \longrightarrow \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O} + 5\text{H}_2\text{O}$ , at  $14.90^{\circ}$ , 8.93 mm.; at  $20^{\circ}$ , 12.93 mm.; at  $24.92^{\circ}$ , 19.10 mm.; and at  $30^{\circ}$ , 27.05 mm.

The dissociation pressure-temperature curves for sodium arsenate show a transition at about  $22^{\circ}$  between the hepta- and the dodecahydrate.

The heats of hydration of the same reactions have been calculated at several temperatures by the aid of the Clapeyron-Clausius and the Nernst equation.

The specific heats of the two hydrates of sodium arsenate have been approximately determined.

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## LXXXV.—The Ternary System Zinc Oxide-Zinc Chloride-Water.

By HAROLD CECIL HOLLAND.

IN the literature some 16 different oxychlorides of zinc are described (see, e.g., "Gmelins Handbuch der anorganischen Chemie," 1924, "Zink," p. 175; Dietrich and Johnston, *J. Amer. Chem. Soc.*, 1927, 49, 1419), but only a few need be cited in detail. From solubility determinations of zinc oxide in aqueous zinc chloride solutions,

Driot (*Compt. rend.*, 1910, **150**, 1426) inferred the existence of  $\text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 6\text{H}_2\text{O}$  and  $\text{ZnCl}_2 \cdot \text{ZnO} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , both of which he isolated. By treating diamminozinc chloride,  $\text{ZnCl}_2 \cdot 2\text{NH}_3 \cdot \text{H}_2\text{O}$ , with hot water, André (*ibid.*, 1882, **94**, 903, 1524; 1888, **106**, 854) obtained an oxychloride to which he gave the formula  $\text{ZnCl}_2 \cdot 8\text{ZnO} \cdot 10\text{H}_2\text{O}$ ; and by adding water to a syrupy solution of zinc chloride, he obtained a compound described as  $\text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 8\text{H}_2\text{O}$ , which was also prepared by Perrot (*Bull. Soc. chim.*, 1895, **13**, 975; 1901, **25**, 786) by adding water to the anhydrous salt.

There is little doubt that several of the supposed oxychlorides are mixtures and not chemical individuals, for analyses of solid phases are necessarily vitiated either by the retention of mother-liquor or by decomposition during washing. It was therefore decided to carry out a phase-rule investigation of the system in order to determine the formulæ of any oxychlorides which might exist in stable equilibrium with solutions.

Although the system is a three-component one, Jänecke's method of representation (*Z. physikal. Chem.*, 1908, **51**, 32; 1911, **71**, 1) was preferred to the triangular method. The compositions of the solid phases were found by Schreinemaker's "residue" method (*Z. physikal. Chem.*, 1893, **11**, 76).

#### EXPERIMENTAL.

The reagents used in the preparations and analyses were of a high standard of purity, and all volumetric apparatus was standardised before use. Chloride was estimated by the Volhard method with *N*/10-silver nitrate and *N*/20-potassium thiocyanate, and zinc by titration with potassium ferrocyanide, a concentrated sulphuric acid solution of diphenylbenzidine being used as indicator (Cane and Cady, *J. Amer. Chem. Soc.*, 1927, **49**, 356): fresh indicator solution had to be made every few weeks in order to get the best results. All solutions were standardised in triplicate and checked fortnightly.

The composition of the mixtures was arranged so as to give only a small amount of solid phase. At first they were prepared from zinc oxide and hydrochloric acid, but, as the most concentrated acid contains only 19.1 equivs. % of hydrogen chloride, the majority were prepared from zinc oxide and chloride and water. By adding some of the water and the zinc oxide in the form of a paste, followed by the hydrochloric acid or zinc chloride dissolved in the remainder of the water, a mixture was obtained free from lumps. If any lumps were present, the mixture, while still hot, was shaken so that the fine precipitate of oxychloride was held in suspension during transference to another bottle, which was then sealed and placed in a rotary shaker in a thermostat at  $25^\circ \pm 0.1^\circ$  or at  $50^\circ \pm 0.05^\circ$ . After the



required period of shaking, the bottle was placed in a clamp at the side of the thermostat to allow the precipitated oxychloride to settle. Some of the clear solution (5, 10, or 25 c.c. as convenient) was drawn off in a pipette and transferred to a weighing bottle; from the weights, the densities of the solutions were obtained. The solid was separated from most of the solution on a Hoesch funnel, and a weighed sample was taken (during filtration the solid was not allowed to become dry, as this would cause change in composition); for the concentrated mixtures at 25° and for all at 50°, the solid was obtained by transferring the remainder of the mixture to a weighing bottle at the temperature concerned, allowing the precipitate to settle, and then drawing off the supernatant liquid. The samples were washed into standard flasks, acidified with dilute sulphuric acid to dissolve oxychlorides, and analysed. From the weights of zinc and chlorine in a known weight of solution or residue the amounts of zinc chloride and oxide and hence of water were obtained.

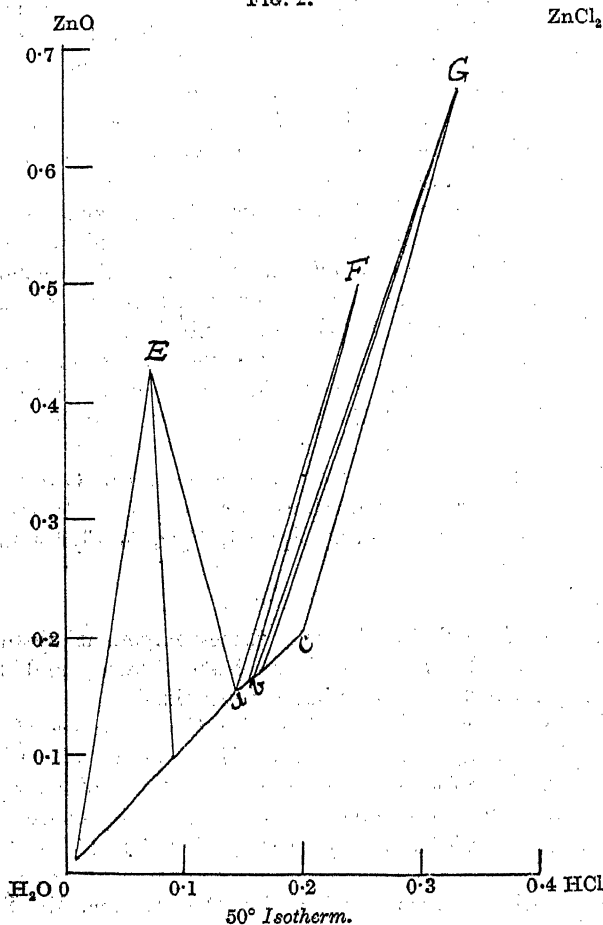
Data at 25°.						
No.	Solution.			Residue.		
	<i>D.</i>	<i>x.</i>	<i>y.</i>	<i>x.</i>	<i>y.</i>	
1	1.004	0.001	0.001	0.020	0.117	E
2	1.056	0.009	0.009	0.016	0.077	
3	1.185	0.033	0.034	0.039	0.107	
4	1.194	0.034	0.035	0.039	0.102	
5	1.270	0.049	0.050	0.052	0.112	
6	1.379	0.075	0.078	0.073	0.115	
7	1.461	0.094	0.097	0.089	0.144	
8	1.552	0.113	0.119	0.108	0.162	
9	1.630	0.134	0.142	0.126	0.173	
10	1.646	0.137	0.145	0.128	0.178	
11	1.692	0.146	0.155	0.140	0.197	E; F
12	1.699	0.151	0.163	0.167	0.221	
13	1.707	0.155	0.165	0.172	0.231	F
14	1.723	0.162	0.169	0.177	0.231	
15	1.731	0.165	0.173	0.183	0.245	G
16	1.737	0.163	0.172	0.183	0.227	
17	—	0.172	0.177	0.189	0.226	
18	1.776	0.184	0.193	0.215	0.294	
19	1.793	0.191	0.196	0.201	0.231	G
20	1.794	0.195	0.198	0.211	0.252	
21	1.835	0.202	0.209	0.211	0.243	
22	1.873	0.222	0.230	0.231	0.270	
23	1.900	0.245	0.252	0.262	0.331	
24	1.971	0.264	0.269	0.266	0.299	

Data at 50°.						
1	1.050	0.009	0.009	0.018	0.075	E
2	1.452	0.091	0.095	0.091	0.116	
3	—	0.143	0.153	0.141	0.166	
4	—	0.144	0.153	0.161	0.214	F
5	1.689	0.154	0.161	0.167	0.211	
6	1.711	0.159	0.167	0.175	0.211	G
7	1.713	0.160	0.168	0.177	0.215	
8	1.716	0.165	0.171	0.192	0.248	
9	1.816	0.200	0.205	0.211	0.245	



In the tables the compositions of the solutions and residues are given in terms of  $x$  and  $y$ , the solid phase being shown by the letter corresponding to the intersection of the tie lines in the diagrams; thus  $E = \text{ZnCl}_2 \cdot 5\text{ZnO} \cdot 8\text{H}_2\text{O}$ ;  $F = \text{ZnCl}_2 \cdot \text{ZnO} \cdot 2\text{H}_2\text{O}$ ;  $G = \text{ZnCl}_2 \cdot \text{ZnO} \cdot \text{H}_2\text{O}$ .

FIG. 2.



Since the time of shaking required for the mixtures to reach equilibrium was dependent on the concentration, two complexes (Nos. 3 and 4) of similar composition were prepared. Although one of these was shaken at 25° for 24 hours and the other for 72 hours, the same solid phase was present in each case, showing that for mixtures of this or higher concentration one day's shaking was sufficient. When several very dilute mixtures were shaken for only

3 days, the conjugation lines did not intersect at a point; but when two such complexes (Nos. 1 and 2) were shaken for 21 days, these lines intersected those of other complexes at a definite point *E* (Fig. 1) corresponding to  $\text{ZnCl}_2, 5\text{ZnO}, 8\text{H}_2\text{O}$ , showing that 3 days' shaking was insufficient. This compound is the same as that obtained by André and by Perrot (*loc. cit.*). As the solution of complex 1 having this solid phase had  $x = y = 0.001$ , it is clear that the range of existence of zinc oxide or hydroxide in contact with solutions containing zinc chloride must be very small.

No evidence was obtained for the existence of the solid,  $\text{ZnCl}_2, \text{ZnO}, 1\frac{1}{2}\text{H}_2\text{O}$ , reported by Driot (*loc. cit.*). As the curve *ab* was increasing at the expense of the others with decrease in temperature, it is quite probable that his solution coincided with the transition point of the curve so that his solid was a mixture of  $\text{ZnCl}_2, \text{ZnO}, 2\text{H}_2\text{O}$  and  $\text{ZnCl}_2, \text{ZnO}, \text{H}_2\text{O}$ . This explanation is strengthened by the fact that he reported only one solution having the solid phase  $\text{ZnCl}_2, \text{ZnO}, 1\frac{1}{2}\text{H}_2\text{O}$  in equilibrium.

At  $50^\circ$ , the diagram (Fig. 2) was of the same form as at  $25^\circ$ , the only difference being that the area *Gcb* had encroached upon the area *Fba*, showing that  $\text{ZnCl}_2, \text{ZnO}, \text{H}_2\text{O}$  can exist in stable equilibrium with solutions containing less zinc chloride than at  $25^\circ$ .

It is of interest that several other elements of Group II of the periodic system give oxychlorides corresponding with two of those now found for zinc: e.g.,  $\text{CaCl}_2, \text{CaO}, 2\text{H}_2\text{O}$ ,  $\text{MgCl}_2, \text{MgO}, \text{H}_2\text{O}$ , and  $\text{CdCl}_2, \text{CdO}, \text{H}_2\text{O}$ .

#### Summary.

1. Equilibria existing in the three-component system  $\text{ZnO}-\text{ZnCl}_2-\text{H}_2\text{O}$  at  $25^\circ$  and  $50^\circ$  have been studied, and the compositions of the stable solid phases determined.

2. Evidence has been obtained for the existence of two new oxychlorides of zinc, viz.,  $\text{ZnCl}_2, \text{ZnO}, 2\text{H}_2\text{O}$  and  $\text{ZnCl}_2, \text{ZnO}, \text{H}_2\text{O}$ ; and only one of those formerly described, viz.,  $\text{ZnCl}_2, 5\text{ZnO}, 8\text{H}_2\text{O}$ , exists in stable equilibrium in the range of concentrations used.

3. The same series of solid phases was found at  $25^\circ$  as at  $50^\circ$ .

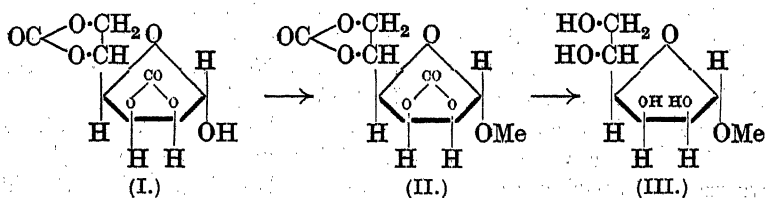
In conclusion, I wish to thank Dr. Denham and Mr. Packer for their interest in this work.

CANTERBURY COLLEGE, NEW ZEALAND. [Received, January 28th, 1930.]

LXXXVI.—Crystalline  $\alpha$ -Methylmannofuranoside ( $\gamma$ -Methylmannoside). Part I.

By WALTER NORMAN HAWORTH and CHARLES RAYMOND PORTER.

UNTIL very recently the synthesis of homogeneous forms of the  $\gamma$ -alkylhexosides had not been possible owing to the lack of appropriate experimental methods. Latterly it has been shown, however, that the crystalline  $\alpha$ - and  $\beta$ -forms of ethylglucofuranosides ( $\gamma$ -ethylglucosides) are obtainable through the sugar carbonates (Haworth and Porter, J., 1929, 2796). A further example of this mode of synthesis is now communicated from which it is seen that crystalline  $\alpha$ -methylmannofuranoside (the  $\alpha$ -form of  $\gamma$ -methylmannoside) is derivable from mannose dicarbonate (Haworth and Porter, this vol., p. 151). The mannose dicarbonate (mannofuranose dicarbonate) (I) undergoes methylation with either diazomethane or methyl iodide and silver oxide and yields the crystalline *methylmannofuranoside dicarbonate* (II). Elimination of the carbonate residue from the latter by the agency of barium hydroxide leads to the formation of the desired crystalline  $\alpha$ -methylmannofuranoside (III).



This substance is hydrolysed with much greater rapidity than the normal  $\alpha$ -methylmannopyranoside, although it is slightly more stable towards *N*/100-hydrochloric acid than the corresponding glucofuranoside. The physical properties of this new five-atom ring form of methylmannoside are compared with those of the pre-existing six-atom ring form which was prepared by Fischer and Beensch (*Ber.*, 1896, 29, 2927).

	M. p.	$[\alpha]^{20}_D$
$\alpha$ -Methylmannofuranoside .....	118—119°	+113°
$\alpha$ -Methylmannopyranoside .....	190—191	+ 79

In the following paper by Haworth, Hirst, and Webb the chemical properties of the new methylmannoside are described and the proof of its constitution (III) is adduced. It is expected that further experiments which are being conducted will lead to the isolation of the stereoisomeric  $\beta$ -methylmannofuranoside.

## EXPERIMENTAL.

*Methylation of Mannofuranose Dicarbonate.*—(a) *With diazomethane.* Diazomethane obtained from 0.5 c.c. of nitrosomethylurethane was distilled together with 4 c.c. of dry ether into 0.5 g. of mannose dicarbonate dissolved in 4 c.c. of dry dioxan (containing a trace of ether) which had been cooled to  $0^{\circ}$ . The cooling was continued during 2 hours. The solution acquired a yellow colour, gas was evolved, and a small amount of yellow syrup separated. By pouring off the solution and allowing it to evaporate at the ordinary temperature, about 0.1 g. of a crystalline material was obtained, m. p.  $170$ – $172^{\circ}$ , identical with the methylmannofuranoside dicarbonate obtained in the following way.

(b) *With methyl iodide and silver oxide.* Mannose dicarbonate (0.4 g.) was dissolved in methyl iodide containing a little acetone and small amounts of silver oxide were added at intervals during  $\frac{1}{2}$  hour, whilst the solution was heated below the boiling point. Prolonged contact with large excesses of silver oxide is harmful. The solution was filtered and the residue was extracted with boiling acetone. The original filtrate and the acetone extracts were evaporated and the residue was again treated with the methylating agents as before. The filtrate from the second treatment yielded on evaporation 0.15 g. of a crystalline product, sparingly soluble in ethyl acetate and obtainable from this solvent as colourless crystals, m. p.  $172$ – $173^{\circ}$  (decomp.) (Found: C, 43.75; H, 4.3; OMe, 12.2.  $C_9H_{16}O_8$  requires C, 43.9; H, 4.1; OMe, 12.6%).

The methylmannofuranoside dicarbonate did not reduce Fehling's solution, but gave a precipitate of barium carbonate on being warmed with barium hydroxide solution. It did not undergo rapid hydrolysis with *N*/10-hydrochloric acid; but after being heated with *N*-hydrochloric acid at  $90^{\circ}$ , it gave a product which rapidly reduced Fehling's solution. It showed  $[\alpha]_{D}^{25} + 87^{\circ}$ ;  $[\alpha]_{5461}^{25} + 98^{\circ}$  (c, 2.45 in acetone).

*$\alpha$ -Methylmannofuranoside.*—The above dicarbonate, dissolved in a little acetone, was warmed gently with excess of barium hydroxide solution. Barium carbonate was precipitated, and after removal of the excess of barium hydroxide by means of carbon dioxide the filtrate was evaporated at  $45^{\circ}$ ; the residue was extracted with ethyl acetate and then with methyl alcohol. Evaporation of either of these extracts gave crystals (yield, 95% of the theoretical). This product, recrystallised from methyl alcohol containing ether, formed colourless needles, m. p.  $118$ – $119^{\circ}$ , showing  $[\alpha]_{D}^{25} + 113^{\circ}$  (c, 1.1 in water);  $[\alpha]_{D}^{25} + 117^{\circ}$ ;  $[\alpha]_{5780}^{25} + 123^{\circ}$ ;  $[\alpha]_{5461}^{25} + 137^{\circ}$  (c, 0.8 in methyl alcohol) (Found: C, 43.25; H, 7.5; OMe, 16.1.  $C_7H_{14}O_6$  requires C, 43.25; H, 7.2; OMe, 16.0%).

$\alpha$ -Methylmannofuranoside is readily soluble in water or alcohol but sparingly soluble in ethyl acetate. It undergoes hydrolysis with *N*/100-hydrochloric acid during a period of 2 hours. Its m. p. is depressed on admixture with  $\alpha$ -methylmannopyranoside.

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### LXXXVII.—Crystalline $\alpha$ -Methylmannofuranoside ( $\gamma$ -Methylmannoside). Part II.

By WALTER NORMAN HAWORTH, EDMUND LANGLEY HIRST, and  
JOHN IVOR WEBB.

WHILE the preceding research was in progress, leading to the synthesis of crystalline  $\alpha$ -methylmannofuranoside from mannose dicarbonate, we were also engaged on the preparation of the same product by a more direct procedure: the condensation of mannose with methyl alcohol in the presence of 1% hydrogen chloride. The neutralised solution yielded a syrup, which was separated from unchanged mannose by solution in ethyl acetate. During the evaporation of this solvent from the extract a copious crop of crystalline  $\alpha$ -methylmannofuranoside separated in a yield of 30%, even though the solution had not been nucleated intentionally with a specimen of the mannofuranoside from the preceding synthetic preparation. This occurrence was repeated as frequently as we performed the mannose-methyl alcohol condensation, and it became evident that, once a nucleus was available,  $\alpha$ -methylmannofuranoside could be obtained almost as readily as  $\alpha$ -methylmannopyranoside (normal  $\alpha$ -methylmannoside). We have therefore been able to isolate considerable quantities of this new substance and have instituted a complete investigation of its properties.

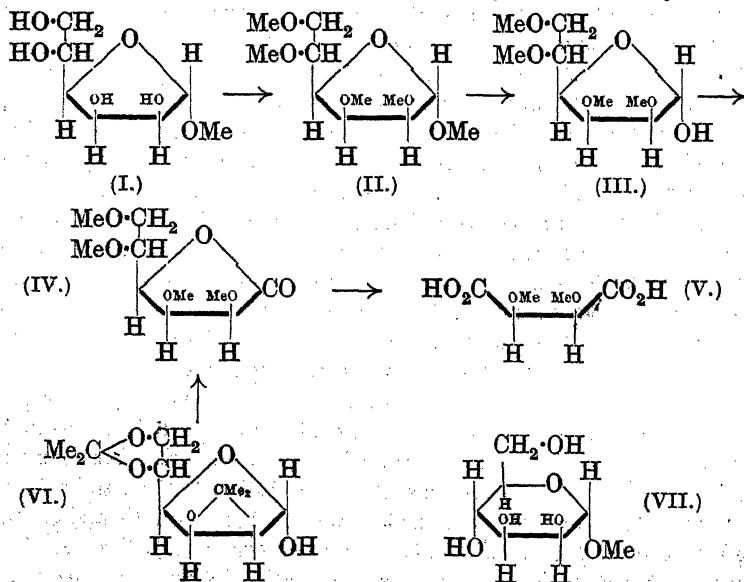
This novel variety of  $\alpha$ -methylmannoside is shown to possess the five-atom ring constitution of a furanoside and it therefore falls into line, both in chemical behaviour and in structure, with other  $\gamma$ -sugar derivatives (compare Haworth and Porter, *J.*, 1929, 2796, and earlier papers). It is hydrolysed completely to mannose on being heated at 100° during 2 hours with *N*/100-hydrochloric acid. The velocity coefficient was calculated to be  $k = 0.015$  (mins. and decimal logarithms), whereas the corresponding six-atom ring form or  $\alpha$ -methylmannopyranoside shows a velocity coefficient  $k = 0.0002$

(Phelps and Hudson, *J. Amer. Chem. Soc.*, 1926, **48**, 503). The pyranoside is, indeed, little affected by heating for this period with acid of this dilution and requires many hours' heating at  $100^\circ$  even with  $N/10$ -acid for complete hydrolysis.

In contact with 15% alkali at  $60^\circ$  the  $\alpha$ -methylmannofuranoside is unaffected during  $1\frac{1}{2}$  hours and is quantitatively recovered after this treatment. It may be handled and preserved in the laboratory without its undergoing any change and requires the observance of no special precautions.

$\alpha$ -Methylmannofuranoside (I) undergoes acetylation to give a crystalline *tetra-acetyl* derivative, which may be contrasted with the previously known three forms of *tetra-acetyl* methylmannoside (compare Dale, *J. Amer. Chem. Soc.*, 1924, **46**, 1050).

Methylation with methyl sulphate and alkali effects a quantitative conversion of (I) into the crystalline *tetramethyl*  $\alpha$ -methylmannofuranoside (II). The tetramethyl derivative (II) is very slightly more stable than the initial unmethylated mannoside, and on being heated at  $100^\circ$  during 8 hours with  $N/100$ -hydrochloric acid it is completely transformed into the free methylated sugar, *tetramethyl mannofuranose* (III). Under identical conditions tetramethyl  $\alpha$ -methylmannopyranoside undergoes little, if any, hydrolysis. Oxidation of (III) with bromine water yielded the crystalline



2:3:5:6-tetramethyl  $\gamma$ -mannonolactone (IV). This lactone had already been prepared from mannose-diacetone (VI) by Goodyear



and Haworth (J., 1927, 3136), who determined its structure by oxidative degradation to *i*-dimethoxysuccinic acid (V), identified through its crystalline ester or methylamide.

These experimental results furnish a proof of the constitution of the new  $\alpha$ -methylmannofuranoside (I) and demonstrate the presence of a five-atom ring. From a parallel series of transformations the six-atom ring structure of  $\alpha$ -methylmannopyranoside (normal  $\alpha$ -methylmannoside) has been derived.

These observations are the more significant in view of the work of Irvine and Burt (J., 1924, 125, 1343), who have recorded the isolation, by the same procedure that we have adopted, of a liquid specimen of  $\gamma$ -methylmannoside. They have ascribed to it exceptional properties. They reported that  $\gamma$ -methylmannoside has only a transient existence and undergoes spontaneous conversion into  $\alpha$ -methylmannopyranoside (VII). We have found, on the contrary, that the  $\gamma$ -mannoside can be preserved indefinitely, without suffering any change. They also observed that  $\gamma$ -methylmannoside changes its ring structure during methylation and is partly converted into tetramethyl  $\alpha$ -methylmannopyranoside. We differ from this view inasmuch as we have observed a quantitative conversion of the  $\gamma$ -mannoside (I) into its crystalline tetramethyl derivative (II) without ring displacement, either by means of methyl sulphate and alkali or of methyl iodide and silver oxide.

These discrepancies are traceable to the statement by Irvine and Burt that, in the initial condensation of mannose with methyl-alcoholic hydrogen chloride, "almost one-half of the sugar was recovered unchanged, the remainder being converted into the new  $\gamma$ -form of methylmannoside." By making this initial assumption they were led to a mistaken view of the nature of their products. As might have been deduced from general principles, this reaction does not give exclusively  $\gamma$ -methylmannosides. Apart from the unchanged mannose which is obtained, extraction of the neutralised product with ethyl acetate yields a mixture of at least four modifications of methylmannoside which were originally present in the acidified methyl-alcoholic solution before its neutralisation. The proportions of these in the neutralised product are not affected on its being kept, nor do the four under-mentioned mannosides undergo interconversion when they are individually isolated. As indicated in the experimental section, we have recovered from this ethyl acetate extract (a) crystalline  $\alpha$ -methylmannopyranoside (VII), (b) the corresponding  $\beta$ -methylmannopyranoside (as its crystalline tetra-acetate), (c) crystalline  $\alpha$ -methylmannofuranoside (the  $\gamma$ -mannoside), and have found evidence also of the presence of (d)  $\beta$ -methylmannofuranoside. A corresponding mixture is obtain-

able also by the method originally adopted by Fischer (*Ber.*, 1914, 47, 1980) for the preparation of  $\gamma$ -methylglucoside, the latter furanoside forms being present along with the  $\alpha$ - and  $\beta$ -glucopyranosides.

In view of these facts it is not surprising that preservation of Irvine and Burt's specimen of  $\gamma$ -methylmannoside led to the separation of crystalline  $\alpha$ -methylmannopyranoside from the mixture, or that during subsequent conversions into the tetramethyl derivatives evidence of this pyranose form was repeatedly encountered. Their final product, when freed ultimately from this impurity as they suggest, must also have contained  $\beta$ -methylmannopyranoside.

Other discrepancies are: (1) the figures given for the rate of condensation of tetramethyl  $\gamma$ -mannose with acid methyl alcohol are at variance with those that we have recorded. A few of their figures for the earlier part of the reaction can be regarded as approximate, but only if their time intervals are read as *hours* and not as *minutes*. (2) Irvine and Burt record analytical figures for a "tetramethyl dimannose" which they isolated, but these are in agreement neither with the figures required for this compound nor for any closely related alternative.

The above-mentioned misconceptions have led to some confusion in another connexion. For instance, Hudson (*J. Amer. Chem. Soc.*, 1926, 48, 1434) has been influenced by Irvine and Burt's observations in formulating his views on the ring structure of sugars.

#### EXPERIMENTAL.

*Preparation of  $\alpha$ -Methylmannofuranoside.*—Mannose (10 g.) was dissolved by shaking in cold dry 1% methyl-alcoholic hydrogen chloride (200 c.c.). After 24 hours at 20°, the acid was neutralised with silver carbonate and the neutral solution was evaporated to dryness under diminished pressure in the presence of barium carbonate. The resultant syrup was extracted ten times with cold ethyl acetate by agitation on a mechanical shaker and the combined ethyl acetate extracts were evaporated under diminished pressure. A syrup remained which crystallised spontaneously once a nucleus of  $\alpha$ -methylmannofuranoside (Haworth and Porter, preceding paper) had been introduced into the laboratory. Recrystallisation from methyl alcohol-ether gave pure  $\alpha$ -methylmannofuranoside, m. p. 118–119°,  $[\alpha]_D^{20} + 113^\circ$  in water (c, 1.0). A mixed m. p. with a sample prepared by Haworth and Porter showed no depression. The yield of pure material (six times crystallised) was 4.5 g. from 15 g. of mannose. The mother-liquors from the crystallisations yielded a small quantity (0.2 g.) of  $\alpha$ -methylmannopyranoside, m. p. 190°,  $[\alpha]_D^{20} + 79^\circ$  in water, and it is shown below that they contained also  $\beta$ -methylmannopyranoside.

Control experiments showed that departure from the conditions laid down above resulted in inferior yields of crystalline material. In particular, no advantage could be gained by using heavy concentrations of hydrogen chloride in the initial condensation.

Samples of crystalline  $\alpha$ -methylmannofuranoside were kept for several months in an ordinary stoppered bottle in the laboratory. In no case was there any sign of transformation into the pyranose form (contrast Irvine and Burt, *loc. cit.*) and the m. p. and specific rotation remained unaltered.

*Hydrolysis of  $\alpha$ -Methylmannofuranoside with N/100-Hydrochloric Acid.*—At 100° in N/100-aqueous hydrochloric acid, hydrolysis of  $\alpha$ -methylmannofuranoside was complete in about 2 hours. The course of the reaction was followed polarimetrically :

<i>t</i> (mins.) ...	0	15	30	45	60	75	90	120	135
$[\alpha]_D^{20}$ .....	+113°	72·3°	51·4°	35°	28°	22·6°	18·6°	15·6°	14·8°
								(constant)	

From these figures the velocity coefficient for the unimolecular reaction at 100° was calculated to be  $k = 0.015$  (mins. and decimal logarithms).

*Stability of  $\alpha$ -Methylmannofuranoside in the Presence of Alkali.*—In 15% aqueous sodium hydroxide solution  $\alpha$ -methylmannofuranoside showed  $[\alpha]_D^{20} + 86^\circ$ . This value is lower than that observed for aqueous solutions and a similar difference was found in the case of  $\alpha$ -methylmannopyranoside, which has  $[\alpha]_D^{20} + 79^\circ$  in water and  $[\alpha]_D^{20} + 69^\circ$  in 15% aqueous sodium hydroxide (*c.* 1.3).

The alkaline solution of  $\alpha$ -methylmannofuranoside remained unaltered in rotation after being heated for 90 minutes at 60°. It was then neutralised by passing carbon dioxide through it and was afterwards evaporated to dryness. The residue was extracted with boiling alcohol, and after removal of the alcohol under diminished pressure the mixture of solid and syrup which remained was treated with boiling ethyl acetate. Evaporation of the latter left crystalline  $\alpha$ -methylmannofuranoside (yield, almost quantitative), which after one recrystallisation from methyl alcohol and ether had m. p. 116°. A mixed m. p. with authentic  $\alpha$ -methylmannofuranoside showed no depression.

*Tetra-acetyl  $\alpha$ -Methylmannofuranoside.*—A solution of  $\alpha$ -methylmannofuranoside (1 g.) in pyridine (8 c.c.) and acetic anhydride (10 c.c.) was kept at 0° for 2 days. It was then poured into water (100 c.c.) and the oil which separated was extracted with chloroform. The chloroform solution was shaken with sodium bicarbonate solution until neutral, washed with water, and evaporated under diminished pressure to a syrup, which still contained pyridine. This was removed by distillation in steam at 40°, after which the residue

was dried at  $40^\circ/10$  mm. for 3 hours, giving a syrup which resisted crystallisation. A small sample left on a watch-glass ultimately solidified and after inoculation with this the main portion crystallised completely (yield, 1.8 g.). Recrystallisation from aqueous alcohol gave *tetra-acetyl  $\alpha$ -methylmannofuranoside* as colourless needles, m. p.  $63^\circ$ ,  $[\alpha]_D^{25} + 107^\circ$  in chloroform (c, 1.0). This substance was non-reducing and was soluble in acetone, ether, alcohol, and chloroform, slightly soluble in water and almost insoluble in light petroleum (b. p.  $60-80^\circ$ ) (Found: C, 49.9; H, 6.4; OMe, 8.6;  $\text{CH}_3\cdot\text{CO}$ , 48.0.  $\text{C}_{15}\text{H}_{22}\text{O}_{10}$  requires C, 49.7; H, 6.1; OMe, 8.6;  $\text{CH}_3\cdot\text{CO}$ , 47.5%). The m. p. of *tetra-acetyl  $\alpha$ -methylpyranoside* is also  $63^\circ$ , but in admixture with *tetra-acetyl  $\alpha$ -methylfuranoside* the m. p. was depressed to  $40-45^\circ$ .

*Acetylation of the Syrupy Residues obtained during the Preparation of  $\alpha$ -Methylmannofuranoside.*—The mother-liquors from the crystallisation of  $\alpha$ -methylmannofuranoside were evaporated to dryness under diminished pressure and the syrup which remained was acetylated with pyridine and acetic anhydride in the manner already described. The product was a syrup from which crystalline material separated on the addition of ether. This solid substance (0.4 g. from 15 g. of mannose) after recrystallisation from absolute alcohol showed m. p.  $156^\circ$ , alone or when mixed with *tetra-acetyl  $\beta$ -methylmannopyranoside*. It follows, therefore, that the ethyl acetate extract of the syrup obtained by condensing mannose with cold methyl-alcoholic hydrogen chloride contained  $\beta$ -methylmannofuranoside in addition to  $\alpha$ -methylmannofuranoside and  $\alpha$ -methylmannopyranoside.

After removal of *tetra-acetyl  $\beta$ -methylmannopyranoside* an uncrystallisable syrup remained which probably consisted mainly of *tetra-acetyl  $\beta$ -methylmannofuranoside*.

*Preparation of Tetramethyl  $\alpha$ -Methylmannofuranoside.*—(a) *By means of methyl sulphate.* A solution of  $\alpha$ -methylmannofuranoside (3 g.) in acetone (30 c.c.) and water (10 c.c.) was rendered slightly alkaline and treated at  $50-55^\circ$  with methyl sulphate (40 c.c.) and 30% aqueous sodium hydroxide (70 c.c.), care being taken to avoid the development of acidity. The product (3.6 g.), after remethylation in acetone solution by methyl sulphate (20 c.c.) and 30% aqueous sodium hydroxide (35 c.c.), was distilled, giving *tetramethyl  $\alpha$ -methylfuranoside* (3.2 g.) as a colourless oil, b. p. about  $120^\circ/0.23$  mm., which solidified completely.  $[\alpha]_D^{25} + 97^\circ$  in water (c, 1.0). After recrystallisation from light petroleum (b. p.  $40-60^\circ$ ), the substance had m. p.  $24^\circ$ ,  $[\alpha]_D^{25} + 98.6^\circ$  in water (c, 1.0),  $[\alpha]_D^{25} + 65^\circ$ , equilibrium rotation in 1% methyl-alcoholic hydrogen chloride (Found: C, 53.0; H, 8.9; OMe, 59.5.  $\text{C}_{11}\text{H}_{22}\text{O}_6$  requires C, 52.8; H, 8.8; OMe, 62.0%).

(b) *By means of silver oxide and methyl iodide.* A solution of  $\alpha$ -methylmannofuranoside (3 g.) in methyl alcohol (15 c.c.) was treated in the usual way with methyl iodide (40 c.c.) and silver oxide (20 g.). The product was soluble in methyl iodide and after three further treatments with methyl iodide and silver oxide the methylation was complete. The final product was a syrup which gave on distillation tetramethyl  $\alpha$ -methylmannofuranoside (3.3 g.), b. p. about  $90^\circ/0.05$  mm.,  $n_D^{18}$  1.4441,  $[\alpha]_D^{20} + 98^\circ$  in water (c, 4.0). This solidified completely when cooled in the ice-chest. Recrystallisation from light petroleum gave needles, m. p.  $24^\circ$  alone or when mixed with the material described above;  $[\alpha]_D^{19} + 99^\circ$  in water.

A mixture of tetramethyl  $\alpha$ -methylmannofuranoside, m. p.  $24^\circ$ , and tetramethyl  $\alpha$ -methylmannopyranoside, m. p.  $37^\circ$ , had so low a m. p. that it was liquid at  $5^\circ$ . The two substances were further differentiated by comparing their rates of hydrolysis by  $N/100$ -hydrochloric acid at  $100^\circ$ . The furanose derivative was completely hydrolysed in about 8 hours, whereas the pyranose derivative was scarcely affected under these conditions. The following polarimetric observations were made during the hydrolysis of tetramethyl  $\alpha$ -methylmannofuranoside prepared by method (a) :

<i>t</i> (mins.)	0	30	60	120	180	240	330	390	480
$[\alpha]_D^{20}$	+97.6°	89.2°	82.7°	72.0°	62.0°	55.5°	49.2°	43.6°	42.7°
								(constant)	

A similar experiment was carried out with material made by method (b). Hydrolysis was complete in about 8 hours and the polarimetric observations were in exact agreement with those just given.

*Tetramethyl Mannofuranose.*—A solution of tetramethyl  $\alpha$ -methylfuranoside (2 g.) in  $N/100$ -aqueous hydrochloric acid (50 c.c.) was heated on the water-bath until the specific rotation reached the constant value  $[\alpha]_D^{20} + 43^\circ$  (8 hours). After neutralisation with barium carbonate the solution was evaporated to dryness under diminished pressure and the product was extracted with boiling ether. Removal of the ether left a syrup which on distillation gave *tetramethyl mannofuranose* as a colourless liquid (1.3 g.), b. p.  $124^\circ/0.1$  mm.,  $n_D^{18}$  1.4532,  $[\alpha]_D^{22} + 39^\circ$ , initial value in water (c, 0.54). After 10 minutes, mutarotation was complete and the final equilibrium rotation was  $[\alpha]_D^{22} + 43^\circ$ ;  $[\alpha]_D^{22} + 37^\circ$  in methyl alcohol (c, 0.86) (Found: C, 50.7; H, 8.7; OMe, 51.7.  $C_{10}H_{20}O_6$  requires C, 50.8; H, 8.5; OMe, 52.5%).

The still residue (0.2 g.) deposited a minute quantity of crystalline material which will be the subject of further investigation in view of the known tendency of furanose compounds to undergo auto-condensation.

Tetramethyl mannofuranose condensed readily with cold methyl

alcohol containing 0.25% of hydrogen chloride. The initial specific rotation,  $[\alpha]_D^{25} + 35^\circ$  (c, 0.81) changed to  $31^\circ$  after 2 minutes,  $28^\circ$  (14 mins.),  $22^\circ$  (36 mins.),  $13.5^\circ$  (1 hour),  $3.7^\circ$  ( $1\frac{1}{2}$  hours),  $-2.5^\circ$  ( $2\frac{1}{4}$  hours),  $+6^\circ$  (15 hours),  $+12^\circ$  (17 hours),  $+20^\circ$  (21 hours),  $+31^\circ$  (25 hours),  $45^\circ$  (40 hours),  $59^\circ$  (60 hours),  $63^\circ$  (88 hours),  $67^\circ$  (final constant value after 120 hours, calc. as tetramethyl methylmannofuranoside). The final value is in excellent agreement with that given above for the equilibrium mixture of the  $\alpha$ - and  $\beta$ -forms of tetramethyl methylmannofuranoside ( $+65^\circ$ ). The observations during the earlier stages of the condensation are in agreement with those of Irvine and Burt only if their times are read in hours instead of in minutes. The slower rate of reaction towards the end of the condensation and the lower value of the final rotation recorded by these authors indicate that their product was impure.

*Oxidation of Tetramethyl Mannofuranose.*—Tetramethyl mannofuranose (1.1 g.), dissolved in water (20 c.c.), was treated with bromine (1.5 c.c.) for 3 days at  $35^\circ$ . The reducing action had then disappeared. After removal of the bromine by aeration the solution was neutralised with silver oxide. Charcoal was added to remove colloidal silver and the solution was then filtered. The dissolved silver was next removed by titration with  $N/2$ -aqueous hydrochloric acid and on evaporation of the water under diminished pressure crystalline tetramethyl  $\gamma$ -mannonolactone was obtained (yield, 1.0 g.) which was identical with the lactone previously described by Goodyear and Haworth (*loc. cit.*). After recrystallisation from ether and light petroleum it had m. p.  $108^\circ$ , alone or when mixed with an authentic specimen of tetramethyl  $\gamma$ -mannonolactone,  $[\alpha]_D^{20} + 65^\circ$ , initial value in water (c, 0.87).

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### LXXXVIII.—*Derivatives of Lyxofuranose.*

By HAROLD GRAHAM BOTT, EDMUND LANGLEY HIRST, and  
JAMES ANDREW BUCHAN SMITH.

SINCE the normal variety of trimethyl lyxose obtained by methylating  $\alpha$ -methyl-lyxoside can be transformed successively into a  $\delta$ -lactone and  $\delta$ -trimethoxyglutaric acid (J., 1928, 3147), normal

derivatives of lyxose must belong to the pyranose type of sugar compounds. This conclusion is, however, in direct conflict with the opinions of Phelps and Hudson (*J. Amer. Chem. Soc.*, 1926, **48**, 503; 1928, **50**, 2049), who uphold the view that  $\alpha$ -methyl-lyxoside is furanose in type. The arguments used by these authors are based entirely on optical relationships, and reasons have already been given (*loc. cit.*) for doubting their applicability in the present instance. The question has now been put to a further experimental test by the preparation of derivatives of lyxose which indubitably have the furanose structure. These new substances show no relationship to  $\alpha$ -methyl-lyxoside but are, on the other hand, typical  $\gamma$ -sugar derivatives. Lyxose therefore falls completely into line with all the other aldoses and ketoses which have been examined, in giving a series of "normal" derivatives which are pyranose in type and a series of more labile  $\gamma$ -derivatives which have the furanose structure.

The study of methyl-lyxofuranoside is of particular interest in view of the important claims made by Irvine and Burt (*J.*, 1924, **125**, 1343) concerning the instability of the closely related  $\gamma$ -methylmannoside. The latter substance is said to change spontaneously into the pyranose form and to yield by structural transformation a considerable proportion of the methylated pyranose variety on treatment with methyl sulphate and alkali. On this account we have examined the behaviour of methyl-lyxofuranoside with particular care. No such anomalous properties have been observed. The substance remains unchanged on being kept for prolonged periods, and methylation, either by methyl sulphate or by silver oxide and methyl iodide, proceeds without structural transformation. In view of these observations it seemed unreasonable to suppose that the configurationally related mannose derivative should differ so fundamentally, and experiments were instituted with " $\gamma$ "-methylmannoside in order to decide this point. As a result we are convinced that Irvine and Burt's conclusions are erroneous, and that in fact neither methyl-lyxofuranoside nor methylmannofuranoside suffers ring displacement during methylation. The experimental evidence, in the case of the mannose derivative, is furnished in the preceding paper (Haworth, Hirst, and Webb).

The starting point of the present investigation was methyl-lyxofuranoside (II), which was prepared by the action of cold methyl-alcoholic hydrogen chloride on lyxose (I). The reaction was accompanied by a comparatively rapid rise in specific rotation, followed by a slow fall to a constant equilibrium value. A similar but more rapid series of changes was observed in hot solutions. When the reaction was stopped at the point of maximum rotation,

the product consisted mainly of methyl-lyxofuranoside, but at equilibrium the solution contained mainly normal  $\alpha$ -methyl-lyxoside.

It is well known that similar reactions occur with other reducing sugars and that in certain cases, notably with galactose and arabinose, a rich proportion of the methyl-furanoside is present at equilibrium. Furthermore, the direct methylation of galactose by methyl sulphate and alkali gives a mixture of furanose and pyranose forms and it would be no matter for surprise should conditions be found under which the methylation of glucose by methyl sulphate would yield derivatives of glucofuranose (Whitnah, *J. Amer. Chem. Soc.*, 1929, **51**, 3490). This author apparently believes that structural determinations made by the methylation method may be rendered invalid by the tendency of the free sugars to yield derivatives of both the furanose and the pyranose type. It is therefore necessary to point out that the structures assigned to the methylglucosides and their derivatives do not depend on results obtained by methylating the free sugars, and that in consequence the observations of Whitnah can have no bearing on the different opinions held respectively by Hudson and by Haworth and the present authors concerning the structure of the methylglucosides.

Owing to the excessive solubility of lyxose and its derivatives, pure methyl-lyxofuranoside could not be obtained and the substance was examined in the form of a syrup, which contained both the  $\alpha$ - and the  $\beta$ -form of methyl-lyxofuranoside (75%), together with free lyxose (15%) and methyl-lyxopyranoside (10%). Details of the method of analysis are given in the experimental section. Methyl-lyxofuranoside showed no tendency to change spontaneously into the pyranose form. It was very sensitive to dilute acids, hydrolysis being complete in less than 20 minutes with *N*/15-hydrochloric acid at 95°.

Treatment of the above mixture containing 75% of methyl-lyxofuranoside with methyl sulphate and alkali under conditions which ensured the destruction of free lyxose gave an excellent yield of the fully methylated derivative. This was a liquid which contained *trimethyl methyl-lyxofuranoside* (90%) (III) and *trimethyl methyl-lyxopyranoside* (10%). A mixture of similar composition was obtained by methylation with silver oxide and methyl iodide. It is obvious from these figures that no transformation of furanose derivative into pyranose took place during methylation. *Trimethyl methyl-lyxofuranoside* was very readily hydrolysed by dilute acids and by taking advantage of this property it was possible to obtain *trimethyl lyxofuranose* (IV) almost entirely free from the corresponding pyranose form. This was accomplished by hydrolysing the mixture of normal and  $\gamma$ -trimethyl methyl-lyxosides with *N*/15-



hydrochloric acid at 95°; the trimethyl methyl-lyxopyranoside then remained unaltered and was removed subsequently by fractional distillation. Trimethyl lyxofuranose was isolated as an uncrystallisable liquid with strong reducing properties, which condensed rapidly in the cold with methyl-alcoholic hydrogen chloride. When heated, trimethyl lyxofuranose underwent autocondensation, two molecules uniting with elimination of one molecule of water to give a crystalline non-reducing substance  $C_{16}H_{30}O_9$ , which was shown to be the *hexamethyl* derivative (V) of a non-reducing dipentose containing two lyxofuranose residues. The high value of the specific rotation,  $[\alpha]_D^{20} + 114^\circ$  in water, would appear to show that both glucosidic groups are  $\alpha$ - in configuration. No such autocondensation was observed with trimethyl lyxopyranose (Hirst and Smith, *loc. cit.*) and it is evident that the increased reactivity in the present case is to be ascribed to the presence of the furanose ring structure.

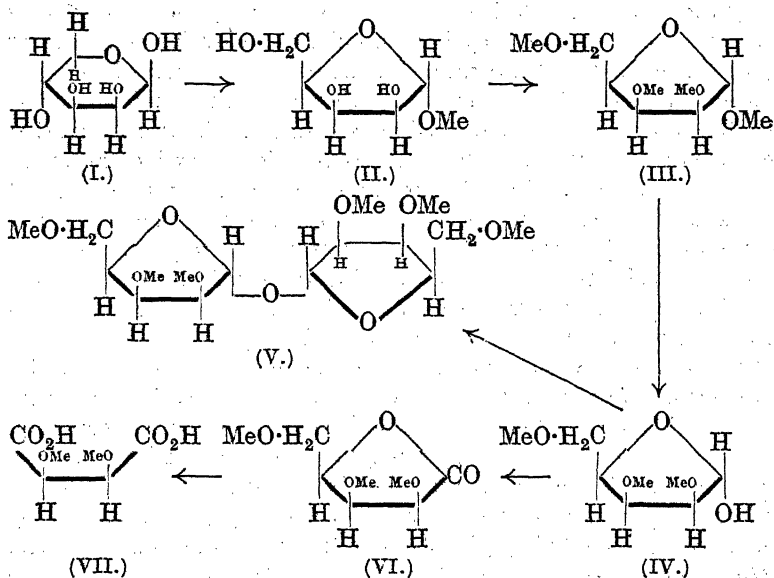
Tetramethyl mannofuranose may be expected to give in a similar way the octamethyl derivative of a disaccharide, and it is possible that this condensation may have been effected by Irvine and Burt (*loc. cit.*, p. 1348). Unfortunately, the evidence provided by these authors is insufficient to show whether the compound formed is similar in type to that described above, and the situation is further complicated by the fact that the product is referred to as tetramethyl dimannose. Even if this name is a misprint for octamethyl dimannose, there still remains the difficulty that the analytical composition of Irvine and Burt's substance corresponded to the formula  $C_{16}H_{26}O_9$ , which they ascribe to tetramethyl dimannose ( $C_{16}H_{30}O_{11}$ ), but which in fact is the formula neither of that substance nor of octamethyl dimannose ( $C_{20}H_{38}O_{11}$ ).

The structure of methyl-lyxofuranoside and its methylated derivatives was established by the preparation of crystalline trimethyl  $\gamma$ -lyxonolactone, obtained by the action of bromine water on trimethyl lyxofuranose. The phenylhydrazide prepared from this lactone was identical with the phenylhydrazide obtained from the trimethyl  $\gamma$ -lyxonolactone which had been prepared previously by epimerising trimethyl  $\gamma$ -xylonolactone (Haworth and Long, J., 1929, 345). Since the structure of the latter substance as a  $\gamma$ -lactone has been established (Haworth and Porter, J., 1928, 611), it follows that " $\gamma$ "-methyl-lyxoside and its derivatives must belong to the furanose class.

The conversion of trimethyl  $\gamma$ -lyxonolactone into the acid proceeded so slowly in aqueous solution that after 1000 hours equilibrium was far from being attained. The conversion of acid into lactone was equally slow, and in consequence only an approximate

value can be given for the proportion of lactone present at equilibrium. This appeared to be about 55%. There is a marked resemblance in these respects between trimethyl  $\gamma$ -lyxonolactone and the stereochemically related tetramethyl  $\gamma$ -mannonolactone (Drew, Goodyear, and Haworth, J., 1927, 1237).

Confirmatory evidence concerning the structure of the trimethyl  $\gamma$ -lyxonolactone was obtained by methylating crystalline  $\gamma$ -lyxonolactone, which had been prepared by oxidising lyxose with bromine water. A comparison of the corresponding phenylhydrazides served to prove the identity of the trimethyl  $\gamma$ -lyxonolactone thus obtained with the material derived from methyl-lyxofuranoside. It will be seen by reference to the experimental section that the methylation of  $\gamma$ -lyxonolactone by silver oxide and methyl iodide is complicated by the tendency of the lactone ring to open in the presence of the water eliminated during the methylation process. From the silver lyxonate then formed, methylated derivatives of methyl lyxonate are obtained.



Still further evidence of the presence of a furanose ring structure in trimethyl methyl-lyxofuranoside was provided by oxidising the substance with nitric acid under conditions which give a quantitative yield of trimethoxyglutaric acid from trimethyl-lyxopyranose. In the present instance the product was mainly *i*-dimethoxysuccinic acid (VII), no trace of which is obtained under these conditions from trimethyl-lyxopyranose. The behaviour during the oxidation,

and the yield of *i*-dimethoxysuccinic acid, which was identified in the form of its crystalline methyl ester, conform exactly with observations recorded during similar oxidation experiments with other methylated furanose derivatives.

When the mixture containing methyl-lyxofuranoside (75%), methyl-lyxopyranoside (10%), and lyxose (15%) was methylated with silver oxide and methyl iodide the main product was, as indicated above, trimethyl methyl-lyxoside, but the process was accompanied by complex oxidative changes which were probably due to the action of silver oxide on the free lyxose present. In addition to trimethyl methyl-lyxoside there was obtained a small amount (4%) of a crystalline substance which analysis showed to be a *methyl* ester of formula  $C_4H_5O_2(OMe)_2 \cdot CO_2Me$ . The possibility that the molecular weight corresponds to some multiple of the simple formula  $C_3H_{14}O_6$  has not been definitely excluded, but the low b. p. of the substance renders such a contingency very improbable. Further experiments are in progress by which it is hoped to determine the structure of this oxidation product.

#### EXPERIMENTAL.

*Methyl-lyxofuranoside*.—Polarimetric observations on a solution of lyxose in 1% methyl-alcoholic hydrogen chloride at 20° showed that the specific rotation increased gradually to a maximum value  $[\alpha]_D^{20} + 72^\circ$  (10 hours) and thereafter decreased to a constant value  $[\alpha]_D^{20} + 42^\circ$  (100 hours). Similar changes took place with more rapidity in hot solutions, and the final product was mainly  $\alpha$ -methyl-lyxoside. Accordingly, lyxose (10 g.) was dissolved in cold 1% methyl-alcoholic hydrogen chloride (300 c.c.) and kept at 20° until the maximum value  $[\alpha]_D^{20} + 73^\circ$  was attained (10 hours). The acid was then neutralised with silver carbonate, and the methyl alcohol removed at 30° under diminished pressure in the presence of a little silver carbonate. The syrup which remained was extracted three times with ethyl acetate at 20° and the extracts were evaporated to dryness at 30°/15 mm. A stiff syrup remained (10 g.) which was perfectly stable when kept in a dry atmosphere free from acid fumes. It contained methyl-lyxofuranoside, methyl-lyxopyranoside and free lyxose.  $[\alpha]_D^{20} + 62^\circ$  in water ( $c = 1.07$ ).

On treatment with *N*/15-hydrochloric acid at 95° rapid hydrolysis of the methyl-lyxofuranoside took place:  $[\alpha]_D^{20} + 62^\circ$  (initial);  $-4^\circ$  (10 mins.);  $-6^\circ$  (20 mins., constant value). The rate of hydrolysis is much more rapid than that of  $\alpha$ -methyl-lyxoside under similar conditions (Phelps and Hudson, *loc. cit.*). The concentration of hydrochloric acid was then increased to *N*/2 and the heating continued. Hydrolysis of the pyranoside was complete in

50 minutes, the final rotation value being  $[\alpha]_D^{20} - 13^\circ$  (calc. as free lyxose), which is very close to the recognised equilibrium value for lyxose.

The amount of free lyxose (15%) was estimated by the Willstätter-Schudel method (*Ber.*, 1918, 51, 780; Goebel, *J. Biol. Chem.*, 1927, 72, 801). Control estimations in which pure lyxose was used gave quantitative results. From the above figures,  $[\alpha]_D + 40^\circ$  being taken as the probable rotation value for the mixture of  $\alpha$ - and  $\beta$ -methyl-lyxopyranosides, it was calculated that the reaction product consisted of free lyxose (15%), methyl-lyxopyranoside (10%), and methyl lyxofuranoside (75%) (Found: OMe, 16.8. Calc. for the above mixture, 15.9%).

*Methylation of Methyl-lyxofuranoside by Methyl Sulphate.*—The mixture described in the previous section was dissolved in acetone (6 g. in 15 c.c.) and treated in the usual manner with methyl sulphate (40 c.c.) and 30% aqueous sodium hydroxide (70 c.c.). The temperature ranged from 55–70° and excess of alkali was added at the beginning of the reaction to destroy the free lyxose. Methylation of the product (5.2 g.) was completed by the use of Purdie's reagents, and the resultant non-reducing syrup (5.2 g.,  $n_D^{17} 1.4477$ ) was distilled, giving a colourless hygroscopic liquid (4.8 g.), b. p. about 90°/0.06 mm.,  $n_D^{17} 1.4457$ ,  $[\alpha]_D^{20} + 52^\circ$  in water ( $c = 0.6$ ),  $[\alpha]_D^{20} + 41^\circ$  in methyl alcohol ( $c = 1.3$ ),  $[\alpha]_D^{20} + 52^\circ$ , equilibrium value after heating with 1% methyl-alcoholic hydrogen chloride. In *N*/15-aqueous hydrochloric acid at 95° hydrolysis of the trimethyl methylfuranosidic portion of the distillate occurred rapidly:  $[\alpha]_D^{20} + 52^\circ$  (initial value);  $+ 48^\circ$  (10 mins.);  $+ 37^\circ$  (30 mins.);  $+ 34^\circ$  (50 mins., constant value). After a further 50 minutes' heating with boiling *N*/2-hydrochloric acid the constant value  $[\alpha]_D^{20} + 31^\circ$  (calculated as trimethyl methyl-lyxoside) was attained, the presence of a small amount of trimethyl methyl-lyxopyranoside being thus indicated. Since trimethyl lyxopyranose has  $[\alpha]_D^{20} - 22^\circ$  (equilibrium value in water) and trimethyl lyxofuranose has  $[\alpha]_D^{20} + 39^\circ$  (equilibrium value in water; see below), it follows that the quantities of *trimethyl methyl-lyxofuranoside* and *trimethyl methyl-lyxopyranoside* in the distillate were about 90% and 10% respectively (Found: C, 52.1; H, 8.6; OMe, 58.5.  $C_9H_{18}O_5$  requires C, 52.4; H, 8.7; OMe, 60.2%).

*Trimethyl Lyxofuranose.*—The mixture (4 g.) of trimethyl methyl-lyxofuranoside and trimethyl methyl-lyxopyranoside was heated at 100° with *N*/15-hydrochloric acid (100 c.c.) until the rotation was  $[\alpha]_D^{20} + 32^\circ$  (1 hour). Under these conditions hydrolysis of the pyranose form would be inappreciable. The solution was neutralised with silver carbonate, filtered, and evaporated under

diminished pressure to a mobile syrup, which was dissolved in ether. After removal of the ether the product was distilled, giving two fractions: (a) a mixture of trimethyl lyxofuranose and unhydrolysed trimethyl methyl-lyxopyranoside (0.83 g.), b. p. about  $95^{\circ}/0.04$  mm.,  $n_D^{18}$  1.4531; (b) *trimethyl lyxofuranose* (2.3 g.), b. p. about  $95^{\circ}/0.04$  mm.,  $n_D^{18}$  1.4580,  $[\alpha]_D^{20} + 39^{\circ}$  in water ( $c = 1.05$ ). This rotation is in good agreement with that obtained for trimethyl lyxofuranose by hydrolysis of a crystalline condensation compound (see below). Furthermore, only trimethyl  $\gamma$ -lyxonolactone was obtained by oxidation of the trimethyl lyxofuranose, which must therefore be free from contamination by its pyranose isomeride (Found: C, 49.8; H, 8.4; OMe, 48.1.  $C_8H_{16}O_5$  requires C, 50.0; H, 8.3; OMe, 48.4%).

Trimethyl lyxofuranose condensed rapidly with methyl alcohol containing 1% of hydrogen chloride at  $20^{\circ}$ :  $[\alpha]_D^{20} + 15^{\circ}$  (4 mins. after dissolution);  $+ 13^{\circ}$  (7 mins.);  $+ 13^{\circ}$  (10 mins.);  $+ 14^{\circ}$  (18 mins.);  $+ 21^{\circ}$  (30 mins.);  $+ 36^{\circ}$  (60 mins.);  $+ 42^{\circ}$  (90 mins.);  $+ 45^{\circ}$  (120 mins.);  $+ 55^{\circ}$  (300 mins.);  $+ 60^{\circ}$  (final equilibrium value). Under similar conditions the condensation of trimethyl lyxopyranose with methyl alcohol was very slow:  $[\alpha]_D^{20} - 9^{\circ}$  (initial value);  $- 12^{\circ}$  (150 mins.);  $- 18^{\circ}$  (3000 mins.). The equilibrium value for the pyranose form is  $[\alpha]_D^{20} + 21^{\circ}$  (Hirst and Smith, *loc. cit.*). In both cases the  $\beta$ -isomeride of the methyl-lyxoside is formed more rapidly than the  $\alpha$ -variety.

Fraction (a) was hydrolysed by boiling for 30 minutes with 2*N*-hydrochloric acid. The distilled product (yield, 70%) was a colourless liquid, b. p.  $95-100^{\circ}/0.03$  mm.,  $n_D^{18}$  1.4605,  $[\alpha]_D^{20} + 16^{\circ}$  in water ( $c = 0.7$ ) (Found: OMe, 46.5. Calc., 48.4%). These figures show that the distillate was trimethyl lyxose containing about 60% of the furanose form ( $[\alpha]_D + 39^{\circ}$ ) and 40% of the pyranose form ( $[\alpha]_D - 22^{\circ}$ ). This is equivalent to the presence of 11% of the pyranose form in the trimethyl methyl-lyxoside, in good agreement with the value 10% previously obtained.

*Condensation of Trimethyl Lyxofuranose to give a Hexamethyl Dipentose.*—When trimethyl lyxofuranose was distilled slowly, only a portion of it could be recovered unchanged. The remainder was a colourless liquid, b. p. about  $160^{\circ}/0.05$  mm., which solidified on cooling. After being drained on porous earthenware and recrystallised from light petroleum (b. p.  $40-60^{\circ}$ ), it gave bunches of needles, m. p.  $77^{\circ}$ , which had no action on boiling Fehling's solution but reduced it strongly after hydrolysis with 3% hydrochloric acid. During the hydrolysis the specific rotation,  $[\alpha]_D^{20} + 114^{\circ}$  (initial value), decreased in 15 minutes to a constant value  $+ 43^{\circ}$  ( $[\alpha]_D^{20} + 41^{\circ}$ , calculated as trimethyl lyxose). The physical and chemical

properties of the new substance indicated that it was the *hexamethyl* derivative of a non-reducing dipentose formed by the autocondensation of two molecules of trimethyl lyxofuranose and this view was confirmed by analysis (Found : C, 52.3; H, 8.0; OMe, 49.3.  $C_{16}H_{30}O_9$  requires C, 52.4; H, 8.2; OMe, 50.8%).

*Trimethyl  $\gamma$ -Lyxonolactone*.—A solution of trimethyl lyxofuranose (1.6 g.) in water (20 c.c.) was treated with bromine (2 c.c.), and kept for 4 days at 35–40°: the reducing properties had then disappeared. The bromine was removed by aeration, an excess of silver oxide was added, and the filtered solution was titrated exactly with hydrochloric acid to liberate the trimethyl lyxonic acid from its silver salt. On evaporation under diminished pressure, followed by heating at 100°/10 mm. to complete the lactonisation, a syrup was obtained which was freed from some inorganic material by solution in ether. On removal of the solvent crystalline trimethyl lyxonolactone was obtained (1.4 g.) which on distillation gave a solid crystalline mass (1.3 g.), b. p. 170°/12 mm., m. p. 37–40°,  $n_D^{20} 1.4569$ ,  $[\alpha]_D^{20} + 82.5^\circ$  in water (initial value, decreasing with extreme slowness). Recrystallisation from ether–light petroleum (b. p. 40–60°) gave needles 4–5 cm. long, m. p. 44°,  $[\alpha]_D^{20} + 82.5^\circ$  in water ( $c = 0.5$ ) (Found : C, 50.5; H, 7.0; OMe, 49.3. Calc. for  $C_8H_{14}O_5$ : C, 50.5; H, 7.4; OMe, 49.0%).

If the trimethyl lyxofuranose had been contaminated with trimethyl lyxopyranose, the specific rotation of the freshly distilled lactone before recrystallisation would have been less than  $[\alpha]_D^{20} + 82^\circ$ , owing to the presence of some trimethyl  $\delta$ -lyxonolactone ( $[\alpha]_D^{20} + 35.5^\circ$ ). The above observations therefore provide additional evidence of the homogeneity of the trimethyl lyxofuranose.

When an ethereal solution of the lactone was heated with the calculated quantity of phenylhydrazine, the corresponding phenylhydrazide was formed. This was washed with ether and on recrystallisation from benzene gave needles, m. p. 140° alone or in admixture with the phenylhydrazide of the acid obtained by the epimerisation of trimethyl xylonolactone (Haworth and Long, *loc. cit.*) (Found : C, 56.2; H, 7.3; N, 9.6; OMe, 31.5. Calc. for  $C_{14}H_{22}O_5N_2$ : C, 56.4; H, 7.4; N, 9.4; OMe, 31.2%).

*Hydrolysis of Trimethyl  $\gamma$ -Lyxonolactone*.—The hydrolysis of the crystalline lactone in aqueous solution was studied polarimetrically. Mutarotation was extremely slow and the behaviour throughout was that of a  $\gamma$ -lactone. The rotation of the free acid was determined in the usual manner by forming the sodium salt, adding the equivalent amount of hydrochloric acid, and determining the rotation immediately.  $[\alpha]^{20} - 21^\circ$  in water ( $c = 0.5$ , calculated as lactone).

*Conversion of lactone into acid.*

Time (hours).	$[\alpha]_D^{20}$ .	% of lactone present.	Time (hours).	$[\alpha]_D^{20}$ .	% of lactone present.
0	+82.5°	100	474	65.0°	83.0
24	80	97.6	551	63.9	82.0
73	77.7	95.3	644	62.3	80.4
145	75.1	92.8	883	57.0	75.3
378	67.1	85.1	1000	56.5	74.8

The conversion of the acid into lactone in aqueous solution proceeded so slowly that equilibrium had not been attained at the end of 500 hours. A direct determination of the proportion of acid and lactone present at equilibrium was therefore impracticable, but an approximate value (55% of lactone) was deduced by extrapolation.

*Conversion of acid into lactone.*

Time (hours).	$[\alpha]_D^{20}$ .	% of lactone present.	Time (hours).	$[\alpha]_D^{20}$ .	% of lactone present.
0	-20.8°	0	75	+6.4°	26
24	-16.0	4.6	140	14.4	34
50	-4.4	16	500	25.6	45

*Methylation of  $\gamma$ -Lyxonolactone.*—Lyxonolactone was prepared from lyxose by heating the sugar with bromine water at 30° for several days. Hydrobromic acid was removed by means of silver oxide and the resulting solution of silver lyxonate was then treated with the exact quantity of hydrochloric acid required to precipitate the silver. Evaporation of the water in a vacuum left a syrup which soon crystallised and pure lyxonolactone, m. p. 109°, was obtained after one recrystallisation from ethyl acetate.

This lactone (2 g.) was methylated in the usual way with Purdie's reagents. Six consecutive treatments were carried out, the addition of methyl alcohol being necessary in the first three in order to effect solution. Fractional distillation of the final product showed that a complex mixture of substances had been formed. The following fractions were taken: (a) 0.14 g., bath temp. 107°/0.04 mm.,  $n_D^{14}$  1.4350; (b) 0.9 g., bath temp. 115°/0.08 mm.,  $n_D^{13}$  1.4372; (c) 0.27 g., bath temp. 125°/0.03 mm.,  $n_D^{12}$  1.4381; (d) 0.72 g., bath temp. 140–150°/0.03 mm.,  $n_D^{11}$  1.4484. The fractions (a), (b) and (c) were esteric in nature and contained substances which were more highly methylated than trimethyl-lyxonolactone, possibly methyl tetramethyl-lyxonate,  $C_{10}H_{20}O_6$ , and methyl trimethyl-lyxonate,  $C_9H_{18}O_6$  [Found for (b): C, 49.5; H, 8.3; OMe, 64.5.  $C_{10}H_{20}O_6$  requires C, 50.8; H, 8.5; OMe, 65.6%.  $C_9H_{18}O_6$  requires C, 48.7; H, 8.1; OMe, 55.8%].

Fraction (d) was mainly trimethyl lyxonolactone (Found: C, 50.4; H, 8.3; OMe, 53.0%). It was not sufficiently pure to crystal-

lise, but the presence of trimethyl  $\gamma$ -lyxonolactone was proved by preparing from it the corresponding phenylhydrazide, which was formed in good yield when an ethereal solution of the liquid was heated on the water-bath with phenylhydrazine. One recrystallisation from benzene sufficed to give the pure phenylhydrazide, m. p.  $140^{\circ}$  (alone or when mixed with the phenylhydrazide of the acid obtained from trimethyl lyxofuranose).

*Oxidation of Trimethyl Methyl-lyxofuranoside with Nitric Acid.*—Trimethyl methyl-lyxofuranoside (2 g.) was heated for 8 hours at  $90^{\circ}$  with nitric acid ( $d$  1.42; 20 c.c.). Evolution of nitrous fumes had then almost ceased. The remaining nitric acid was removed by distillation under diminished pressure at  $50^{\circ}$ , with frequent addition of water. The stiff syrup obtained was boiled for 6 hours with 2% methyl-alcoholic hydrogen chloride. After neutralisation of the acid by silver carbonate the methyl alcohol was removed by distillation under diminished pressure and the product was distilled, giving a colourless liquid (0.9 g.), b. p.  $135\text{--}140^{\circ}/12$  mm. No methyl oxalate could be detected and there was no still residue. The distillate, after nucleation with a crystal of methyl *i*-dimethoxy-succinate, began to crystallise. After being kept for several weeks, the solid was drained on porous tile and recrystallised from ether-light petroleum, giving flat plates (0.4 g.), m. p.  $68^{\circ}$  alone or when mixed with an authentic specimen prepared from *i*-tartaric acid.

*Methylation of Methyl-lyxofuranoside by Purdie's Reagents.*—The crude methyl-lyxofuranoside described above (10 g.) was methylated six times with silver oxide and methyl iodide. The product was distilled, giving 7.9 g., b. p.  $70\text{--}74^{\circ}/0.08$  mm., and 3.5 g., b. p.  $75\text{--}90^{\circ}/0.08$  mm. A small quantity (4%) of a crystalline oxidation product (A) separated from both fractions. This was removed by draining on porous tile, after which the liquid was recovered by extraction with chloroform and redistilled; b. p.  $75^{\circ}/0.1$  mm.,  $n_D^{20}$  1.4431,  $[\alpha]_D^{20} + 41^{\circ}$  in water ( $c = 3.6$ ),  $[\alpha]_D^{20} + 53^{\circ}$  in 1% methyl-alcoholic hydrogen chloride (equilibrium value after being heated at  $100^{\circ}$  for 6 hours). The distillate was mainly trimethyl methyl-lyxofuranoside, but contained also the corresponding pyranoside (15–20%) and probably also a little of the above-mentioned crystalline product (Found: OMe, 56.8%). Hydrolysis with dilute hydrochloric acid gave the corresponding mixture of trimethyl lyxofuranose and trimethyl lyxopyranose. This had b. p.  $95^{\circ}/0.04$  mm.,  $n_D^{20}$  1.4598,  $[\alpha]_D^{20} + 27^{\circ}$  in water ( $c = 3.3$ ) (Found: OMe, 47.5%). Oxidation with bromine water gave the mixed  $\gamma$ - and  $\delta$ -lactones as a liquid, b. p.  $108^{\circ}/0.1$  mm.,  $n_D^{20}$  1.4553,  $[\alpha]_D^{20} + 76^{\circ}$  in water (initial value);  $+ 65^{\circ}$  (23 hours);  $+ 63^{\circ}$  (41 hours);  $+ 58^{\circ}$  (90 hours);  $+ 50^{\circ}$  (200 hours);  $+ 45^{\circ}$  (300 hours);  $+ 41^{\circ}$  (900 hours).



The comparatively rapid fall in rotation during the first 50 hours, followed by the slow change which still persisted after 1000 hours, is characteristic of a mixture of a  $\gamma$ - and a  $\delta$ -lactone. Since the trimethyl  $\gamma$ - and  $\delta$ -lyxonolactones have respectively  $[\alpha]_D^{20} + 82.5^\circ$  and  $[\alpha]_D^{20} + 36^\circ$ , the proportion of  $\delta$ -lactone was about 15%. After some time the trimethyl  $\gamma$ -lyxonolactone crystallised; m. p.  $44^\circ$ . Preparation of the phenylhydrazide from the liquid which drained away from the crystalline  $\gamma$ -lactone gave mainly the phenylhydrazide obtainable from trimethyl  $\delta$ -lyxonolactone.

The crystalline oxidation product (A) was easily soluble in the usual organic solvents, soluble with difficulty in water, and was recrystallised from light petroleum, giving long colourless needles, m. p.  $127-128^\circ$ ,  $[\alpha]_D^{20} + 175^\circ$  in water ( $c = 0.53$ ). The substance was neutral to litmus and had no action on boiling Fehling's solution. The presence of an ester group was proved by titration with hot alkali, and after alkaline hydrolysis the high specific rotation was retained. When the ester was heated for 2 hours at  $80^\circ$  with 3% hydrochloric acid, the rotation decreased to  $0^\circ$ ; the resulting solution, after exact neutralisation with sodium hydroxide, did not reduce boiling Fehling's solution but quickly decolorised neutral permanganate [Found: C, 46.5; H, 6.8; OMe, 45.1;  $\text{CO}_2\text{Me}$ , 28.0.  $\text{C}_4\text{H}_5\text{O}_2(\text{OMe})_2 \cdot \text{CO}_2\text{Me}$  requires C, 46.6; H, 6.8; OMe, 45.1;  $\text{CO}_2\text{Me}$ , 28.6%].

The authors wish to express their thanks to Professor W. N. Haworth, F.R.S., for his interest in this work. They are grateful also to the Department of Scientific and Industrial Research for the award of a maintenance grant to one of them (J. A. B. S.) and to the Chemical Society for a grant which has in part defrayed the cost of the materials.

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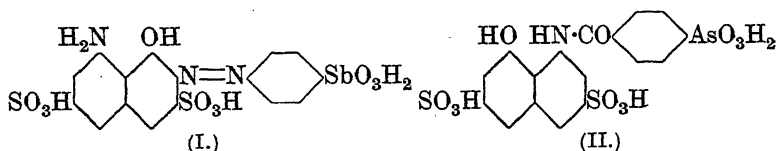
[Received, December 14th, 1929.]

### LXXXIX.—*Trypanocidal Action and Chemical Constitution. Part IX. Aromatic Acids containing an Amide Group.*

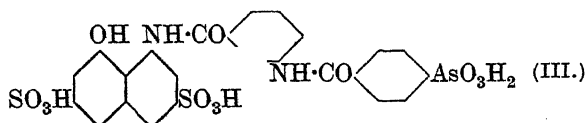
By GEORGE ALECK CROCKER GOUGH and HAROLD KING.

THE activity of the cotton dye (I) on *Trypanosoma equiperdum* in rats (Dunning and Macht, *J. Pharm. Exp. Ther.*, 1928, **32**, 205) suggested to us an investigation of the colourless substance (II),

which would bear to (I) the same relation as Bayer 205 to trypan-red and afridol-violet (compare Balaban and King, J., 1927, 3068).



To facilitate synthesis, antimony was replaced by arsenic. The arsenic analogue of (I) was found to be active but not permanently curative. Arsinous and arsinic acids of type (II) prepared from Freund's acid and H-acid were inactive, even if the substantive character was increased (Balaban and King, *loc. cit.*) by changing the structure to (III). The current theory of the activity of arsinic



acids is that they must first be reduced by living tissues to the much more toxic oxides, and it occurred to us that the amide link might possibly remove these substances out of the range of reduction potential of the mammalian tissues.

Accordingly, *benzamide-p-arsinic acid* (IV) was prepared, but it proved to have a therapeutic activity far exceeding that of *p-amino-*



phenylarsinic acid, the starting point of Ehrlich's series of active arsenicals. This interesting discovery made an extensive study of other benzamidearsinic acid derivatives particularly desirable, since no compound of this type had previously been described. A number of substituted benzarsinic acids are known, but no one has converted these carboxylic acids into their simple amides.

The parent substance, benzoyl chloride *p*-dichloroarsine, lends itself to development in a wide variety of ways, for the lone chlorine atom can be replaced by primary or secondary amino-groups or by simple derivatives of these with formation of a series of amides of the type (V). The following table shows the results obtained when a simple series of aromatic amides was tested on an experimental infection of *Trypanosoma equiperdum* in mice, *T* signifying the maximum dose tolerated, expressed in milligrams per gram of mouse, *C* the minimum curative dose, and *r* the number of days during which the blood stream remained free from trypanosomes.

*Amides of Benz-p-arsinic and -arsinous Acids.*

Type.	$\cdot\text{CO}\cdot\text{NR}_1\text{R}_2$	Arsinic acid.			Arsinous acid.		
		<i>T.</i>	<i>C.</i>	<i>r.</i>	<i>T.</i>	<i>C.</i>	<i>r.</i>
Benzarsinic acid	$\cdot\text{CO}\cdot\text{OH}$	0.2	[inactive]		—	—	—
Amide	$\text{R}_1=\text{H}, \text{R}_2=\text{H}$	1.0	0.3	>30	0.03	0.01	14
Methylamide	$\text{R}_1=\text{Me}, \text{R}_2=\text{H}$	1.0	0.5	>30	0.01	0.0075	>30
Ethylamide	$\text{R}_1=\text{Et}, \text{R}_2=\text{H}$	1.25	0.75	>30	0.0075	0.005	>30
Propylamide	$\text{R}_1=\text{Pr}, \text{R}_2=\text{H}$	0.4	0.2	11	0.005	0.0025	11
isoAmylamide	$\text{R}_1=\text{C}_5\text{H}_{11}, \text{R}_2=\text{H}$	0.1	0.1	6	0.0025	0.0025	9
Dimethylamide	$\text{R}_1=\text{Me}, \text{R}_2=\text{Me}$	0.6	0.5	5	0.01	0.005	5
Diethylamide	$\text{R}_1=\text{Et}, \text{R}_2=\text{Et}$	0.1	[inactive]		0.0025	[inactive]	
Piperidinoamide	$\cdot\text{NR}_1\text{R}_2=\text{C}_5\text{H}_{10}\text{N}$	0.1	[inactive]		0.0025	[inactive]	
Phenylamide	$\text{R}_1=\text{Ph}, \text{R}_2=\text{H}$	0.1	0.05	>30	—	—	—

If it is borne in mind that the aim of this kind of work is to discover a substance in which the margin between *C* and *T* is as wide as possible, and that the substances should be "permanently" curative, i.e., that *r* should be greater than a month, it will be observed that trypanocidal activity falls off in the monosubstituted alkylamides with increasing weight of the substituting group, and very rapidly in the disubstituted amides.

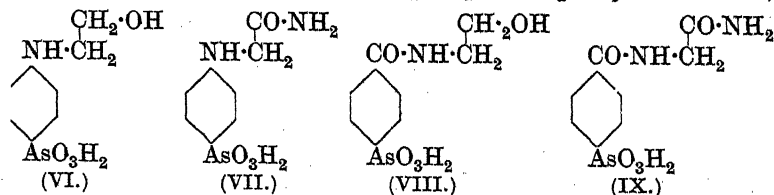
Attention was then directed to the meta-series of amides from benz-*m*-arsinic acid, but they proved to be definitely weaker than those of the para-series.

*Amides of Benz-m-arsinic and -arsinous Acids.*

Type.	$\cdot\text{CO}\cdot\text{NHR}_1$	Arsinic acid.			Arsinous acid.		
		<i>T.</i>	<i>C.</i>	<i>r.</i>	<i>T.</i>	<i>C.</i>	<i>r.</i>
<i>m</i> -Benzarsinic acid	$\cdot\text{CO}\cdot\text{OH}$	1.5	[inactive]		—	—	—
Amide	$\text{R}_1=\text{H}$	0.6	0.4	>30	0.005	0.005	3
Methylamide	$\text{R}_1=\text{Me}$	0.4	0.2	5	0.01	0.0075	>30
isoAmylamide	$\text{R}_1=\text{C}_5\text{H}_{11}$	0.01	[inactive]		—	—	—

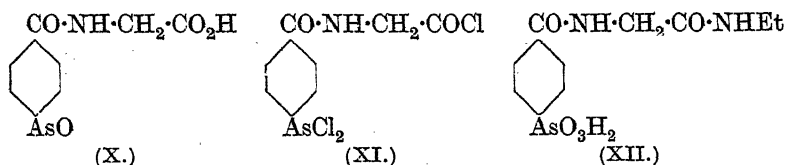
Many of the amides described above, both meta- and para-substituted and containing the arsenic in the quinquevalent state, produced nervous symptoms of chronic poisoning in mice. An attempt was therefore made to prepare derivatives of benzamide-*p*-arsinic acid which would show an equally good therapeutic index without producing any untoward symptoms.

When the modified alkyl groups  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  and  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$  are introduced into the amino-group of *p*-aminophenylarsinic acid,



two valuable trypanocidal agents, etharsenol (VI) and tryparsamide (VII) respectively, are known to be obtained. It was, therefore, of

interest to attempt the preparation of their analogues (VIII) and (IX) from benz-*p*-arsinic acid. Although benzoyl chloride *p*-dichloroarsine readily reacted with  $\beta$ -aminoethyl alcohol with formation of an arsinous acid which on oxidation gave (VIII), attempts to prepare (IX) were not immediately successful. Hippuro-*p*-arsine oxide (X) when subjected to the action of phosphorus pentachloride in the presence of acetyl chloride gave the trichloro-compound (XI), but this on treatment with ammonia under many conditions always regenerated hippuroarsine oxide. When, however, ammonia was replaced by ethylamine, the *ethylamide* of hippuro-*arsinic acid* (XII) was readily obtained.



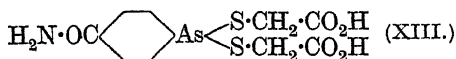
The following table shows the activity of these and some related substances in comparison with benzamide-*p*-arsinic acid. R signifies  $-\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$  and R' the reduced form  $-\text{C}_6\text{H}_4\cdot\text{AsO}_2\text{H}_2$ .

	<i>T.</i>	<i>C.</i>	<i>r.</i>
R·CO·NH <sub>2</sub> .....	1·0	0·3	>30
R·CO·NH·CH <sub>2</sub> ·CH <sub>2</sub> ·OH .....	2·0	1·0	6
R'·CO·NH·CH <sub>2</sub> ·CH <sub>2</sub> ·OH .....	0·01	0·01	>30
R·CO·NH·CH <sub>2</sub> ·CO <sub>2</sub> H .....	1·25	[inactive]	>30
R·CO·NH·CH <sub>2</sub> ·CO·NH <sub>2</sub> .....	>3·0	1·0	>30
R·CO·O·CH <sub>2</sub> ·CH <sub>2</sub> ·NEt <sub>2</sub> .....	2·0	[inactive]	>30

Of this series the ethylamide of hippuroarsinic acid (XII) proved the most useful, and on the highest dose tried there were no nervous symptoms noticeable in mice. The lower homologues of this acid, hippuramide-*p*-arsinic acid and its *N*-methyl derivatives, will be described in a subsequent communication.

Another way of avoiding the undesirable symptoms evoked by benzamide-*p*-arsinic acid would be by use of the corresponding arsinous acid, for since this has more than 30 times the acute toxicity of the acid containing quinquevalent arsenic, and might have a correspondingly high curative power, the amount of arsenic administered would be correspondingly small. Although this arsinous acid produces no nervous symptoms, it is by no means so effective (compare the first table) as the arsinic acid and it occurred to us that it might be possible to render it more effective by esterification with a suitable alcohol. The ester might then be expected to have an increased efficiency, since slow hydrolysis would liberate the toxic arsinous acid over a period of time. For this purpose we chose  $\alpha$ -thiolacetic acid, which had already been condensed with 3-amino-

4-hydroxyphenylarsinous acid by Voegtlin, Dyer, and Leonard (*U.S. Public Health Rep.*, 1923, **38**, 1911). When an aqueous suspension of benzamide-*p*-arsinous acid was boiled with  $\alpha$ -thiolacetic acid, condensation took place rapidly with formation of crystalline *di(carboxymethyl) benzamide-p-thioarsinite* (XIII).



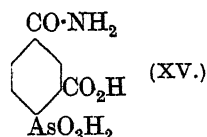
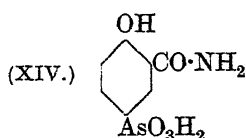
On its maximum tolerated dose, this substance produced no nervous symptoms and it was more effective than the arsenious acid.

	<i>T.</i>	<i>C.</i>	<i>r.</i>
Benzamide- <i>p</i> -arsinous acid .....	0.03	0.01	14
Benzamide- <i>p</i> -thioarsinite .....	0.05	0.03	>30

We had made this compound and had examined its oxidation with iodine when an important paper appeared by Barber (J., 1929, 1020) on the condensation of thiol acids with arsenic acids. We believe, however, that some of the results of this author bear a simpler interpretation than that given by him. Barber observed that the arylthioarsinites in alkaline solution, with sodium hydrogen carbonate, for instance, give an intense nitroprusside reaction which he attributed to the intact arylthioarsinite molecule. In support of this he states that the arylthioarsinites do not undergo hydrolytic fission with alkali, because the alkali-metal salts of the *di(carboxymethyl) arylthioarsinites* can be obtained from strongly alkaline solution. Such a view is, however, untenable. *Di(carboxymethyl) benzamide-p-thioarsinite* (XIII) is soluble in cold sodium hydrogen carbonate solution and gives an intense nitroprusside reaction indistinguishable in tint from that due to  $\alpha$ -thiolacetic acid. The free acid also dissolves sparingly in water and gives the transient blue colour with ferric chloride characteristic of  $\alpha$ -thiolacetic acid. Both these reactions are specific for thiol groups, and indicate partial hydrolysis of the thioarsinites in weakly alkaline solution and even in water. When a feebly alkaline solution of *di(carboxymethyl) benzamide-p-thioarsinite* was treated with one molecular proportion of hydrogen peroxide, benzamide-*p*-arsinic acid was isolated together with unchanged thioarsinite. This result is inconsistent with an exclusive initial addition of oxygen to the arsenic atom of the intact ester molecule, followed by hydrolysis, a process which would seem to follow on Barber's view of the properties of these compounds, but is consistent with oxidation of the hydrolytic products, arylarsinous acid and  $\alpha$ -thiolacetic acid, formed in alkaline solution. The occurrence of some oxidation of the intact ester molecule is not, however, excluded. In further support of the ease of hydrolysis of *di(carboxymethyl) benzamide-*

*p*-thioarsinite is the observation of our biological colleagues, Miss Durham and Miss Strangeways, that at high dilutions trypanosomes exposed to its action are rendered non-infective, a property usually recognised as specific for the arylarsinous acids or oxides.

The effect of introducing a second substituent into the phenyl nucleus of benzamidearsinic acid has been examined in a few cases and others are still under investigation. *Salicylamide-5-arsinic acid* (XIV) and *isophthalamic acid 6-arsinic acid* (XV) have been prepared, but not *isophthalamide-4-arsinic acid*. The toxicities and

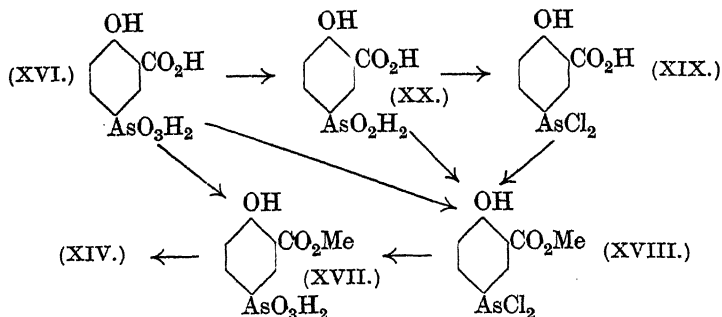


therapeutic activities of these substances compared with some intermediate and allied products are recorded below.

	<i>T.</i>	<i>C.</i>	<i>r.</i>
<i>p</i> -Tolylarsinic acid .....	0.005	[inactive]	
<i>m</i> -Xylarsinic acid .....	0.03	[inactive]	
<i>iso</i> Phthalic acid 4-arsinic acid .....	0.03	[inactive]	
Methyl isophthalate-4-arsinic acid .....	0.3	[inactive]	
<i>iso</i> Phthalamic acid 6-arsinic acid .....	0.05	[inactive]	
Salicylic acid 5-arsinic acid .....	1.5	[inactive]	
Methyl salicylate-5-arsinic acid .....	0.02	[inactive]	
Salicylamide-5-arsinic acid .....	0.75	0.3	5

The preparation of salicylamide-5-arsinic acid and *isophthalamic acid 6-arsinic acid* presents some points of interest. When salicylic acid 5-arsinic acid (XVI) prepared by the Bart-Schmidt reaction from 5-aminosalicylic acid is esterified with methyl-alcoholic sulphuric acid, the degree of esterification increases with the amount of sulphuric acid used. At the same time fission of arsenic as arsenious acid increases so that the most favourable conditions for the esterification are uncertain. If the sulphuric acid is replaced by dry hydrogen chloride, the *methyl ester* (XVII) may again be isolated together with some *methyl salicylate-5-dichloroarsine* (XVIII). The latter substance is formed by loss of labile chlorine atoms which react with the solvent. Similarly in the esterification of *isophthalic acid 4-arsinic acid* by methyl-alcoholic hydrogen chloride in boiling solution, reduction to *methyl isophthalate dichloroarsine* is complete. Indeed, this action of dry hydrogen chloride on arsinic acids appears to be a general one. For the preparation of methyl salicylate-5-arsinic acid (XVII) it is, however, preferable to reduce salicylic acid 5-arsinic acid by sulphurous acid in concentrated hydrochloric acid solution directly to *salicylic acid dichloroarsine* (XIX), as this is more easily isolated than the intermediate product *salicylic acid*

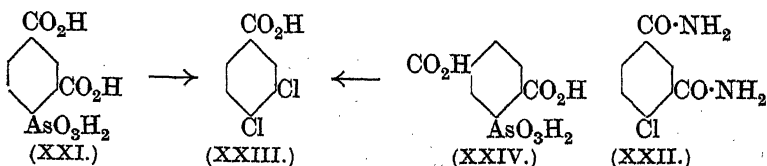
arsinous acid (XX), which separates when the reaction is carried out in dilute hydrochloric acid solution. Salicylic acid dichloro-



arsine (XIX), like salicylic acid arsinous acid (XX), is then readily esterified by methyl-alcoholic hydrogen chloride to methyl salicylate-5-dichloroarsine (XVIII). Careful oxidation of a suspension of this in aqueous sodium hydrogen carbonate at  $0^\circ$  with hydrogen peroxide gives methyl salicylate-5-arsinic acid (XVII), and by the action of ammonia on the ester in dilute methyl alcohol at  $100^\circ$  salicylamide-5-arsinic acid (XIV) is obtained.

The difficulties attending the preparation of *isophthalamide*-4-arsinic acid have not yet been surmounted. When *isophthalic acid* 4-arsinic acid (XXI) is allowed to react with thionyl chloride, it gives almost exclusively the half acid chloride of *isophthalic acid* dichloroarsine, for on treatment with ammonia and oxidation with hydrogen peroxide *isophthalamide* 6-arsinic acid (XV) is obtained.

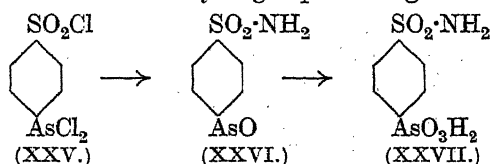
With  $5\frac{1}{2}$  molecular proportions of phosphorus pentachloride, the products isolated are the same *isophthalamide* 6-arsinic acid, 4-chloro*isophthalamide* (XXII), and 3:4-dichlorobenzamide; and with  $6\frac{1}{2}$  molecular proportions, only the last two substances are obtained, the whole of the arsinic acid group having been replaced by chlorine. The constitution of 4-chloro*isophthalamide* follows from its hydrolysis to 4-chloro*isophthalic acid*, and that of 3:4-dichlorobenzamide follows from its hydrolysis to 3:4-dichlorobenzoic acid (XXIII) which was identical with the acid obtained (later communication) by a similar series of reactions from terephthalic acid arsinic acid (XXIV).



When *isophthalic acid 4-arsinic acid* is esterified in synthetic methyl alcohol by saturation with hydrogen chloride at  $0^{\circ}$ , crystalline *methyl isophthalate arsinetetrachloride* separates after a few hours. This tetrachloride dissolves in sodium hydrogen carbonate solution at  $0^{\circ}$  and yields *methyl isophthalate-4-arsinic acid* on acidification. If, however, purified methyl alcohol (wood spirit) is used in the esterification, no separation of an arsinetetrachloride occurs at  $0^{\circ}$ , but when the solution is boiled, reduction takes place with formation of *methyl isophthalate dichloroarsine*, which is isolated as *methyl isophthalate-4-arsinous acid* by pouring the reaction mixture into sodium hydrogen carbonate solution. On oxidation the arsinous acid yields *methyl isophthalate-4-arsinic acid*.

When *methyl isophthalate-4-arsinic acid* is allowed to react with ammonia ( $d$  0.88) at  $0^{\circ}$  for 14 days, the sole product of amidation is the same *isophthalamide acid 6-arsinic acid* as is obtained from the acid chlorides.

The marked influence on the trypanocidal activity of benz-*m*- and -*p*-arsinic acids effected by their conversion into amides, recorded in the foregoing pages, made it desirable to prepare benzenesulphonamide-*p*-arsinic acid. *p*-Sulphophenylarsinic acid had been previously prepared by Hewitt, King, and Murch (J., 1926, 1355) and had been shown to be devoid of activity. By the action of phosphorus pentachloride in boiling carbon tetrachloride solution it was converted into *benzenesulphonyl chloride p-dichloroarsine* (XXV), which on graded hydrolysis with water gave *benzenesulphonyl chloride p-arsenoxide* and *sulphophenylarsinous acid*. By the action of ammonia *benzenesulphonamide-p-arsenoxide* (XXVI) was obtained, and this on treatment with hydrogen peroxide gave *benzenesulphon-*



*amide-p-arsinic acid* (XXVII). With hydrochloric acid, however, the arsinous acid gave *benzenesulphonamide-p-dichloroarsine*. The trypanocidal activity of some of these compounds was examined with the following results:

	<i>T.</i>	<i>C.</i>	<i>r.</i>
Sulphophenyl- <i>p</i> -arsinic acid .....	0.5	[inactive]	
Benzenesulphonamide- <i>p</i> -arsinic acid .....	>1.5	1.0	16
Benzenesulphonamide- <i>p</i> -arsenoxide .....	0.03	0.01	>30

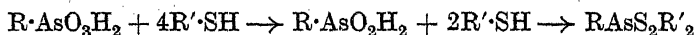
#### *Therapeutic Considerations.*

Analysis of the results described in the foregoing pages reveals some underlying principles of considerable interest. The first of



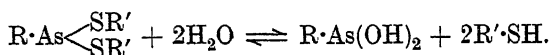
these is the important influence of the amide group in converting trypanocidally inactive carboxylic and sulphonic acids into substances of marked activity. It was known that phenylglycineamide-*p*-arsinic acid (tryparsamide) could cure both experimental and clinical trypanosomiasis, but the significance of the aliphatically bound amide group was obscure, since data on analogous derivatives were lacking. In this communication it has, however, now been demonstrated that benz-*m*- and -*p*-arsinic acids, hippuro-*p*-arsinic acid, salicylic acid 5-arsinic acid, *p*-sulphophenylarsinic acid, and the corresponding arsinous acids were tested, are quite inactive on experimental trypanosomiasis in mice; and yet, when they are converted into the corresponding amides, trypanocidal activity appears in every case. The interpretation is simple. Following the injection of these arsinic or arsinous acids into the blood stream as soluble sodium salts, two main processes become operative, excretion and reduction. Those substances containing solubilising groups such as carboxyl or sulpho, whether they are reduced to the arsinous acids or not, will remain as soluble salts by reason of the carboxyl or sulpho-groups, and their excretion will be rapid. On the other hand, those containing amide groups will also be excreted, though possibly at a slower rate, so long as they contain the arsinic acid group and can form neutral soluble salts. When, however, reduction to the arsinous acid has taken place, they will no longer form neutral salts and will, accordingly, be liberated in the colloidal state as free arsinous acids by hydrolysis at the  $p_H$  of the blood stream, and will not be excreted as such. The mechanism of the reduction process and subsequent events may also be pictured from analogous reactions *in vitro*.

It is known that hydrogen sulphide is a very powerful reducing agent, having in fact a reduction potential negative to the hydrogen electrode. It is, therefore, not surprising to find, as Barber (*loc. cit.*) does, that various thiol derivatives of aliphatic acids can reduce arsinic to arsinous acids, condensation then taking place between the arsinous acids and excess of the thiol compound with production of arylthioarsinites, operations which can take place at the ordinary



temperature in neutral solution. It is very probable that similar processes operate in mammalian tissues, for there is abundant evidence of the presence of thiol compounds in tissues, and some for their being concerned in oxidative-reductive processes. That the excess of thiol groups should act as receptors for the arsinous acid group is also very probable; it was, in fact, foreshadowed by Ehrlich many years ago (*Ber.*, 1909, 42, 42). The occurrence of

arsenic in hair after arsenic medication is possibly a manifestation of the property. The further important point, however, now emerges from our experiments, that the arylthioarsinites are slowly hydrolysed even in neutral solution with regeneration of small amounts of arsinous acids.



The view we advanced in the preceding communication of this series (Gough and King, J., 1928, 2432), that the arsinic acids are "reduced to the reactive oxides, and stored as such by condensation in a reversible form," thus receives experimental support. The arylthioarsinites would be formed from proteins of all degrees of complexity containing sulphydryl groups, and would in general escape excretion, and the continuous production of minute amounts of highly toxic arsinous acids by hydrolysis of such complex thioarsinites in the tissues, maintained over an extended period, would be responsible for the complete disappearance of the trypanosomes with resultant cure.

Lastly, the wide variation in the chemotherapeutic efficiency of arsenicals with change of constitution might be ascribed to difference in the ease of reduction of the arsinic to the arsinous acid, difference in the ease of condensation of the arsinous acid with thiol complexes, and difference in the ease of hydrolysis of such complexes. In fact, the striking results obtained for the series of similarly constituted amides shown in the first table (p. 671), where other factors affecting trypanocidal activity might be expected to be reasonably constant, support such a view. As this table shows, introduction of methyl into the amide group causes a diminution in activity, and this diminution is intensified by increase in the size of the alkyl group or by the introduction of more than one. Introduction of weakly positive alkyl groups will cause a drift of electrons towards the arsenic atom relative to the effect of the unsubstituted amide group, and this will be reflected (*a*) in a diminished ease of reduction of the arsinic acid, since the oxygen atom will be more firmly held, and (*b*) in a decreased tendency to co-ordinate with hydroxyl (Gough and King, *loc. cit.*, p. 2429), since the arsenic atom has become more negative, with resultant increased difficulty of hydrolysis. Both properties would lead to diminished trypanocidal activity, as is actually found.

We are deeply indebted to Miss F. M. Durham and Miss W. I. Strangeways for the whole of the biological findings recorded in this paper.

## EXPERIMENTAL.

*Derivatives of Naphthylaminesulphonic Acids.*

1-Amino-3 : 6-disulpho-8-naphthol-7-azobenzene-4'-arsinic Acid (compare D.R.-P. 212018).—4-Aminophenylarsinic acid (8.7 g.) in 80 c.c. of 2*N*-hydrochloric acid was treated at 0° with 3.0 g. of sodium nitrite in 30 c.c. of water and then added slowly to 13.6 g. of H-acid in 150 c.c. of 3*N*-sodium hydroxide solution. After being kept at 0° for 45 minutes, the solution was made just acid to Congo-paper by addition of concentrated hydrochloric acid. After 12 hours the deep-coloured solid was collected on porous plate and purified by solution in the minimum volume of boiling water and addition of one-fifth of that volume of concentrated hydrochloric acid. This operation was repeated three times and gave finally 2.8 g. of homogeneous brick-red needles (Found : loss at 105°, 8.0.  $C_{16}H_{14}O_{10}N_3S_2As \cdot 2\frac{1}{2}H_2O$  requires  $H_2O$ , 7.6%. Found in dried acid : As, 13.3.  $C_{16}H_{14}O_{10}N_3S_2As$  requires As, 13.7%). When pure, this acid requires over 12 parts of boiling water for solution, but will not crystallise therefrom on cooling. It is, however, almost completely precipitated by addition to the solution of one-fifth of its volume of 32% hydrochloric acid.

1-Benzamido-3 : 6-disulphonaphthalene-4'-arsinous Acid.—Freund's acid (9 g.), dissolved in *N*-sodium hydroxide (90 c.c.), was treated in presence of benzene (10 c.c.) with three successive portions of benzoyl chloride *p*-dichloroarsine (each 5.7 g.) in benzene (13 c.c.). *N*-Sodium hydroxide (30 c.c.) was added concurrently with vigorous shaking. After removal of the benzene, the liquid was diluted with an equal volume of water and acidified to Congo-paper and the precipitated benz-*p*-arsinous acid (9.8 g.) was removed. The liquid was then concentrated to 100 c.c. and a further small amount of benz-*p*-arsinous acid removed (0.1 g.). After addition of concentrated hydrochloric acid (7 c.c.) and keeping for 2 hours at -5°, clusters of fine needles separated (11.2 g.). These were recrystallised by solution in warm water (24 c.c.) and addition of concentrated hydrochloric acid (4 c.c.) (Found : loss at 140°, 7.5.  $C_{17}H_{13}O_9NS_2AsNa \cdot H_2O$  requires  $H_2O$ , 6.5% for conversion into oxide. Found in anhydrous oxide : As, 13.1; Na, 4.2.  $C_{17}H_{11}O_8NS_2AsNa$  requires As, 13.5; Na, 4.1%).

1-Benzamido-3 : 6-disulphonaphthalene-4'-arsinic Acid.—The crude arsinous acid (7 g.), dissolved in water (35 c.c.), was treated with the calculated amount of 30% hydrogen peroxide in water (14 c.c.). The solution, which became warm and slightly brown on oxidation, was neutralised to litmus-paper, warmed at 50° for  $\frac{1}{2}$  hour, and evaporated under reduced pressure to 20 c.c., and the reaction

adjusted to neutrality to Congo-paper. The solution was then heated to  $100^{\circ}$  and, after addition of concentrated hydrochloric acid (3 c.c.), allowed to cool. The resultant paste of fine rectangular needles (5.7 g.) was removed and recrystallised by solution in the minimum volume of boiling water, followed by the addition of concentrated hydrochloric acid (5.5 c.c.) (Found: loss at  $140^{\circ}$ , 12.6; As, 12.7; Na, 3.8.  $C_{17}H_{13}O_{10}NS_2AsNa \cdot 3H_2O$  requires  $H_2O$ , 11.9 for conversion into the dioxide; As, 12.3; Na, 3.8%).

*1-Benzamido-3:6-disulpho-8-naphthol-4'-arsinous Acid*.—H-Acid (6.8 g. monosodium salt +  $1.5H_2O$ ), dissolved in *N*-sodium hydroxide (20 c.c.), was treated with 0.5 c.c. portions of a solution of benzoyl chloride *p*-dichloroarsine (11.4 g.) in benzene (20 c.c.) with vigorous shaking. *N*-Sodium hydroxide (40 c.c.) was added concurrently at such a rate as to maintain a slightly alkaline reaction. The liquid was made acid to Congo-paper, and the precipitated benzarsinous acid (3.3 g.) removed. The filtrate was concentrated (to 10.4 c.c., to 76 c.c., and until salt began to separate) at  $50^{\circ}$  and the three successive crops were united and boiled with water (25 c.c.) containing norit. The undissolved portion yielded a further quantity of benzarsinous acid (1.8 g.), and the filtrate, on the addition of concentrated hydrochloric acid, gave the desired *amide* (11.4 g.). This was recrystallised three times from hot water (28, 21, and 16.5 c.c.), concentrated hydrochloric acid (2 c.c.) being added to the clear solution in each operation (Found: loss at  $140^{\circ}$ , 23.8; As, 10.3; Na, 3.8.  $C_{17}H_{13}O_{10}NS_2AsNa \cdot 8H_2O$  requires  $H_2O$ , 23.2 for conversion into the arsenious oxide; As, 10.7; Na, 3.3%).

*1-Benzamido-3:6-disulpho-8-naphthol-4'-arsinic Acid* (II).—A slightly alkaline solution of the foregoing arsinous acid (11.3 g. in 150 c.c.) was treated with the calculated amount of hydrogen peroxide, kept for  $\frac{1}{2}$  hour, and concentrated to 95 c.c. The mass of stout needles which separated was dissolved by warming, and the solution made acid to Congo-paper. On cooling, the desired *arsinic acid* (8.8 g.) separated in fine needles. This, together with a further amount (1.4 g.) obtained from the mother-liquor, was recrystallised from water (18 c.c.) with the addition of concentrated hydrochloric acid (4 c.c.) (Found: loss at  $150^{\circ}$ , 24.8; As, 10.0.  $C_{17}H_{13}O_{11}NS_2AsNa \cdot 10H_2O$  requires  $H_2O$ , 24.6 for conversion into the dioxide; As, 10.2%).

*1-Benzamido-m-benzamido-3:6-disulpho-8-naphthol-4''-arsinous Acid*.—A solution of 1-*m*-aminobenzamido-8-naphthol-3:6-disulphonic acid (7.1 g.; Balaban and King, J., 1927, 90) in *N*-sodium hydroxide (40 c.c.) with benzene (10 c.c.) was treated with 0.5 c.c. portions of a solution of benzoyl chloride *p*-dichloroarsine (9.8 g.) in benzene until it no longer gave a red colour when diazotised and

coupled with  $\beta$ -naphthol. After removal of the benzene, the liquid was made slightly acid to Congo-paper, filtered from benzarsinous acid (1.4 g.), and evaporated (to 35 c.c.) at 50°. After further filtration the liquid was saturated with sodium chloride and kept at 0° for 12 hours, and the crude *arsinous acid* was then removed and recrystallised from water (140 c.c.) by the addition of concentrated hydrochloric acid at 50° until a slight turbidity was produced. The desired product separated in characteristic bunches of needles (Found: loss at 140°, 18.5; As, 9.0.  $C_{24}H_{18}O_{11}N_2S_2AsNa \cdot 8H_2O$  requires  $H_2O$ , 19.9 for conversion into the oxide; As, 9.2%).

*1-Benzamido-m-benzamido-3:6-disulpho-8-naphthol-4''-arsinic Acid (III).*—The foregoing arsinous acid (3.5 g.) was dissolved in half-saturated sodium hydrogen carbonate solution (50 c.c.) and oxidised by the addition of 30% hydrogen peroxide (0.6 g.) in water (10 c.c.). After  $\frac{1}{2}$  hour, the liquid was made slightly acid to Congo-paper and saturated with sodium chloride. The precipitated *arsinic acid* was collected and crystallised by solution in water (18 c.c.) at 50°, followed by the addition of concentrated hydrochloric acid (10 c.c.). On keeping, light pink needles of the required acid separated. These were again recrystallised by the use of water (15 c.c.) and hydrochloric acid (8 c.c.) (Found: loss at 140°, 29.1; As, 7.5.  $C_{24}H_{18}O_{12}N_2S_2AsNa \cdot 14H_2O$  requires  $H_2O$ , 28.7 for conversion into the oxide; As, 8.0%).

#### *Derivatives of p- and m-Benzarsinic Acids.*

*Benzamide-p-arsenious Oxide.*—Benzoyl chloride *p*-dichloroarsine (15 g.), dissolved in benzene (20 c.c.), was added slowly to 2*N*-aqueous ammonia (200 c.c.) and benzene (10 c.c.) with vigorous shaking. The precipitate, which began to separate after the first few additions, was collected (11 g.). Acidification of the filtrate gave benzarsinous acid (1.1 g.). For purification the crude product was reprecipitated from 2*N*-sodium hydroxide. This *arsenious oxide*, like all the benzalkylamidoarsenious oxides examined, is insoluble in dilute ammonia and cold sodium hydrogen carbonate solution and does not show any visible crystalline structure (Found: N, 6.4; As, 35.7.  $C_7H_6O_2NAs$  requires N, 6.6; As, 35.6%).

*Di(carboxymethyl) Benzamide-p-thioarsinite (XIII).*—A suspension of the above arsenious oxide (1 g.) in boiling water (19 c.c.) was treated with  $\alpha$ -thiolacetic acid (1.1 g.). The solid rapidly passed into solution and on cooling, fine needles (1.7 g.) of *di(carboxymethyl) benzamidethioarsinite*, m. p. 168–169°, separated. It was recrystallised from boiling water (25 c.c.) containing a small amount of thiolacetic acid (Found: As, 20.1.  $C_{11}H_{12}O_5NS_2As$  requires As, 19.9%). When titrated with iodine in the presence of starch, one

molecule of this substance reacts rapidly with four atoms of iodine in agreement with the formation of disulphidoacetic acid and benzamide-*p*-arsinic acid. When a slightly alkaline solution of the thioarsinite (0.41 g.) in sodium hydrogen carbonate solution was treated with half the quantity of hydrogen peroxide (0.13 g.) requisite for complete oxidation, the original material (0.21 g.) and benzamide-*p*-arsinic acid (0.08 g.) were readily isolated.

The parent thioarsinite is readily hydrolysed, for a solution in aqueous sodium hydrogen carbonate gives an intense nitroprusside reaction and an aqueous solution of the free acid gives a transient blue colour with ferric chloride. These reactions are not due to traces of  $\alpha$ -thiolacetic acid contaminating the crystalline material, since they are given by odourless samples of the thioarsinites which have been exposed to the air for several months.

*Benzamide-p-arsinic Acid* (IV).—The corresponding arsenious oxide (11 g.) was suspended in water (70 c.c.) containing hydrogen peroxide (5.7 g. of 30% "perhydrol") and heated on the water-bath until solution was complete. On cooling, large plates of *benzamide-p-arsinic acid* (9.1 g.) separated, which were recrystallised from water (58 c.c.). The arsinic acid (7.1 g.) thus obtained is unmelted at 300° and forms crystalline barium and calcium salts (Found: N, 5.5; As, 30.4.  $C_7H_8O_4NAs$  requires N, 5.7; As, 30.6%).

*Benzomethylamide-p-arsinous acid* was prepared similarly by means of aqueous methylamine (Found: As, 30.6.  $C_8H_{10}O_3NAs$  requires As, 30.3%). The corresponding *arsinic acid* crystallised from water in stout needles, unmelted at 300° (Found: N, 5.7.  $C_8H_{10}O_4NAs$  requires N, 5.4%).

*Benzodimethylamide-p-dichloroarsine*.—Benzoyl chloride *p*-dichloroarsine was allowed to react with aqueous dimethylamine in the usual way. After removal of benzene, addition of concentrated hydrochloric acid gave a copious precipitate of small rectangular plates of *benzodimethylamide-p-dichloroarsine*, m. p. 192° (Found: As, 25.4.  $C_9H_{10}ONCl_2As$  requires As, 25.5%). On oxidation in alkaline solution it gave *benzodimethylamide-p-arsinic acid*, m. p. 216–218°, which crystallised from water in small plates (Found: N, 5.0.  $C_9H_{12}O_4NAs$  requires N, 5.1%).

*Benzethylamide-p-arsinous acid* was obtained when benzoyl chloride *p*-dichloroarsine in benzene was allowed to react at 0° with anhydrous ethylamine in benzene, and the mixture treated with acidified water (Found: As, 29.3.  $C_9H_{12}O_3NAs$  requires As, 29.2%). On oxidation it gave star-shaped leaflets of *benzethylamide-p-arsinic acid*, unmelted at 300° (Found: N, 5.3.  $C_9H_{12}O_4NAs$  requires N, 5.1%).

*Benzodiethylamide-p-dichloroarsine* was prepared by digesting

benzoyl chloride *p*-dichloroarsine and diethylamine in boiling benzene, the gum remaining on evaporation being dissolved in caustic alkali and extracted with ether to remove diethylamine. On addition of excess of concentrated hydrochloric acid to the residue *benzodiethylamide-p-dichloroarsine*, m. p. 185—186°, was obtained as a crystalline precipitate (Found: Cl, 21.8; As, 23.2.  $C_{11}H_{14}ONCl_2As$  requires Cl, 22.0; As, 23.3%). On oxidation it gave *benzodiethylamide-p-arsinic acid*, stout prisms, m. p. 193—195°, from water (Found: N, 4.9.  $C_{11}H_{16}O_4NAs$  requires N, 4.7%).

*Benzo-n-propylamide-p-arsenious oxide* was prepared similarly to the monoethyl derivative (Found: As, 29.6; N, 5.6.  $C_{10}H_{12}O_2NAs$  requires As, 29.6; N, 5.5%). On oxidation it gave clusters of needles of *benzo-n-propylamide-p-arsinic acid*, unmelted at 300° (Found: N, 4.8.  $C_{10}H_{14}O_4NAs$  requires N, 4.9%).

*Benzisoamylamide-p-arsenious oxide* was prepared similarly (Found: As, 26.5.  $C_{12}H_{16}O_2NAs$  requires As, 26.7%). On oxidation it gave crystalline *benzisoamylamide-p-arsinic acid*, almost insoluble in boiling water but, unlike the lower homologues, easily soluble in ethyl acetate and in ethyl and methyl alcohols (Found: N, 4.7.  $C_{12}H_{18}O_4NAs$  requires N, 4.4%).

*Benzopiperidide-p-dichloroarsine* was prepared from the reactants in boiling benzene solution. The residue obtained on removal of the solvents was treated with chloroform in the presence of concentrated hydrochloric acid. The chloroform solution on concentration and addition of light petroleum gave *benzopiperidide-p-dichloroarsine*, needles, m. p. 166—167° (Found: As, 22.4.  $C_{12}H_{14}ONCl_2As$  requires As, 22.5%). It gave *benzopiperidide-p-arsinic acid*, needles, m. p. 230° (Found: As, 23.8.  $C_{12}H_{16}O_4NAs$  requires As, 24.0%).

*Benzo-β-hydroxyethylamide-p-arsenious Oxide*.—Benzoyl chloride *p*-dichloroarsine (7.1 g.), dissolved in benzene (20 c.c.), was allowed to react with a solution of ethanolamine (2.3 g.) in water (20 c.c.) and benzene (5 c.c.) with the concurrent addition of 2*N*-sodium hydroxide (50 c.c.) in a manner similar to that used in the preparation of benzamide-*p*-arsenious oxide. When the reaction was complete the liquid was made slightly acid to litmus, saturated sodium hydrogen carbonate solution (50 c.c.) added, and the solid (6 g.) removed. *Benzo-β-hydroxyethylamide-p-arsenious oxide* is obtained in this way free from benzarsinous acid. It crystallises from a large volume of hot water or better from a mixture of ethyl alcohol and water in clusters of small needles (Found: As, 29.5.  $C_9H_{10}O_3NAs$  requires As, 29.4%). On oxidation it gave *benzo-β-hydroxyethylamide-p-arsinic acid* (VIII), glistening leaflets, m. p. 180° (efferv.) (Found: N, 4.7.  $C_9H_{12}O_5NAs$  requires N, 4.8%).

*Hippuryl Chloride p-Dichloroarsine* (XI).—Treatment of benzoyl-

glycine-*p*-arsenious oxide (Hugounenq and Morel, *J. Pharm. Chim.*, 1913, 7, 383) with a chloroform solution of thionyl chloride did not give the required results. When a method similar to that used by Fischer (*Ber.*, 1905, 38, 605) for the preparation of hippuryl chloride was used, a crude hippuryl chloride *p*-dichloroarsine was readily obtained. The arsenious oxide (1 g.), suspended in freshly distilled acetyl chloride, was shaken with phosphorus pentachloride (2.5 g.) for 1 hour. The amorphous product (2.1 g.) was collected and washed with light petroleum (10 c.c.). Although attempts to purify it failed (Found: Cl, 34.6.  $C_9H_7O_2NCl_3As$  requires Cl, 31.1%), it could be used successfully for the next process.

*Benzoylglycine-ethylamide-p-arsinic Acid* (XII).—Finely powdered hippuryl chloride *p*-dichloroarsine (5.3 g.) was added to a solution of anhydrous ethylamine (4.2 g.) in dry ether (75 c.c.) cooled in a freezing mixture. After 2 hours, the solid was collected, ground with water (50 c.c.), and washed with sodium hydrogen carbonate solution. The product was suspended in hot water and treated with 30% hydrogen peroxide, and the resultant solution evaporated at 50° to 10 c.c. On cooling, elongated leaflets, which formed clusters, separated. These were recrystallised from boiling water (34 c.c.) (yield, 6.1 g.). *Benzoylglycine-ethylamide-p-arsinic acid* thus obtained melts at 270° (decomp.) (Found: N, 8.6.  $C_{11}H_{15}O_5N_2As$  requires N, 8.5%).

*Benzoylglycine-n-propylamide-p-arsenious oxide* was prepared by the interaction of *n*-propylamine (0.4 g.) and hippuryl chloride *p*-dichloroarsine (0.3 g.) in ether (30 c.c.). The product was amorphous and very similar to its lower homologue (Found: N, 9.1.  $C_{12}H_{15}O_3N_2As$  requires N, 9.0%).

*β-Diethylaminoethyl Benzoate-p-arsinic Acid*.—A solution of β-diethylaminoethanol (11.1 g.) and benzoyl chloride *p*-dichloroarsine (7.1 g.) in benzene (50 c.c.) was cautiously prepared and refluxed for 1½ hours. The suspension of waxy solid was shaken with water (50 c.c.), and the benzene removed under reduced pressure. After neutralisation of the residue with sodium hydrogen carbonate solution, the thick oil was dissolved by addition of ether (150 c.c.). The ethereal extract was dried but, after removal of the ether, all attempts to crystallise the crude arsinous acid, either as such or as the dichloroarsine hydrochloride, failed. In this behaviour it resembles its stovaine analogue (Fourneau and Ochslin, *Bull. Soc. chim.*, 1912, 11, 912). The oil (4.7 g.) was therefore oxidised directly to the arsinic acid by means of hydrogen peroxide in aqueous suspension. The resultant solution was evaporated to dryness, and the residue extracted with boiling alcohol (20 c.c.); cautious addition of dry ether gave fine needles of β-diethylamino-



*ethyl benzoate-p-arsinic acid*, m. p.  $186^{\circ}$  (decomp.) (Found : N, 3.7.  $C_{13}H_{20}O_5NaAs$  requires N, 3.8%).

*Benzoyl Chloride m-Dichloroarsine*.—*m*-Benzarsinous acid was prepared from *m*-aminobenzoic acid (50 g.) by the Bart reaction, the intermediate arsinic acid being reduced without isolation in the solid state, by sulphur dioxide in the presence of hydrochloric acid; the yield varied between 35 g. and 52 g. In preparing the trichloride, it was found that chilling the light petroleum extract (250–300 c.c.) of the distillation residue of the action of thionyl chloride on the arsinous acid in chloroform gave fluffy bunches of needles of *benzoyl chloride m-dichloroarsine* (27 g.), m. p.  $54$ – $55^{\circ}$  (Found : Cl, 37.6.  $C_7H_4OCl_2As$  requires Cl, 37.3%).

*m-Benzarsinous Acid*.—The foregoing chloride (5 g.) was dissolved by warming in 2*N*-sodium hydroxide (20 c.c.), and the solution made slightly acid to Congo-paper with hydrochloric acid. (Owing to the ease of formation of the dichloroarsine, excess of hydrochloric acid must be avoided.) A white mass of microscopic crystals of *m-benzarsinous acid* (4.2 g.) separated (Found : As, 32.3.  $C_7H_7O_4As$  requires As, 32.6%).

*Benzoic Acid m-Dichloroarsine*.—*m*-Benzarsinous acid (1 g.) was dissolved in a boiling mixture of water (12 c.c.), ethyl alcohol (9 c.c.), and concentrated hydrochloric acid (7 c.c.), and a further quantity (4 c.c.) of hydrochloric acid cautiously added. An oil tended to separate on cooling, but was prevented by addition of more alcohol or by seeding with crystals of an externally crystallised sample. The resultant mass of white prisms was removed and washed with concentrated hydrochloric acid (Found : Cl, 26.6.  $C_7H_5O_2Cl_2As$  requires Cl, 26.6%). This substance is more readily hydrolysed than many other dichloroarsines.

*Benzamide-m-arsenious Oxide*.—This substance (12 g.) was prepared from the corresponding acid chloride and ammonia by the method employed for the *p*-isomeride and obtained as a micro-crystalline powder (Found : As, 35.4.  $C_7H_6O_2NaAs$  requires As, 35.6%).

*Benzamide-m-dichloroarsine*.—The foregoing arsenious oxide (1 g.) was dissolved in a hot mixture of 3*N*-hydrochloric acid (5.5 c.c.) and ethyl alcohol (5.5 c.c.), and concentrated hydrochloric acid (8 c.c.) slowly added at the boiling point. On cooling, large prisms of *benzamide-m-dichloroarsine*, m. p.  $76$ – $80^{\circ}$ , separated (Found : Cl, 26.7.  $C_7H_6ONCl_2As$  requires Cl, 26.7%). On oxidation in alkaline solution it gave *benzamide-m-arsinic acid*, rhombic plates, unmelted at  $300^{\circ}$  (Found : N, 5.6.  $C_7H_5O_4NaAs$  requires N, 5.7%).

*Benzomethylamide-m-arsenious Acid*.—This substance (5.2 g.) was obtained in the same way as its *p*-isomeride (Found : As, 30.6.

$C_8H_{10}O_3NAS$  requires As, 30.9%): on oxidation in alkaline solution it gave fine rods of *benzomethylamide-m-arsinic acid*, m. p.  $238^\circ$  (efferv.) (Found: N, 5.5.  $C_8H_{10}O_4NAS$  requires N, 5.4%).

*Benzisoamylamide-m-arsinic Acid*.—When the corresponding arsinous acid was prepared by the same method as that used for the *p*-isomeride, a thick brown gum was obtained which remained partly solid after being kept for several days at  $0^\circ$ . Accordingly this impure product was oxidised directly to the *arsinic acid* by treatment with 30% hydrogen peroxide (3 g.) and 2*N*-sodium hydroxide solution (30 c.c.). The *arsinic acid* obtained resembled the *p*-isomeride in its solubilities in various solvents. It was finally purified by fourfold precipitation from its solution in saturated sodium hydrogen carbonate solution (yield, 6 g. from 7.1 g. of benzoyl chloride *m*-dichloroarsine) (Found: N, 4.5.  $C_{12}H_{18}O_4NAS$  requires N, 4.4%).

*Nuclear-substituted Benzamidearsinic Acids. Derivatives of Salicylic Acid 5-Arsinic Acid.*

*5-Nitrosalicylic Acid*.—The methods for the preparation of this acid have been critically examined by Raiziss and Proskouriakoff (*J. Amer. Chem. Soc.*, 1922, **44**, 784), but neither the method adopted by these authors nor those recorded in the literature gave satisfactory results. After many trials the following conditions were found to give the 5-nitro-acid consistently in 42% yield. Salicylic acid (100 g.) was slowly added (compare Meldola, Foster, and Brightman, *J.*, 1917, **111**, 536) to a solution of nitric acid (100 c.c., *d* 1.42) in water (800 c.c.) heated on the water-bath. The contents first became dark, but on further heating (3.5 hours) a light yellow powder of 5-nitrosalicylic acid remained at the bottom of the flask. On cooling, a mass of fine needles also separated consisting chiefly of the 3-nitro-isomeride. The total solid was collected and boiled with water (400 c.c.), the liquid filtered hot, and the residue washed with boiling water (100 c.c.). The insoluble portion consisted of the 5-nitro-acid, m. p.  $228^\circ$ . 5-Aminosalicylic acid was prepared from the nitro-acid by the method of Weil, Traun, and Marcel (*Ber.*, 1922, **55**, 2665).

*Salicylic Acid 5-Arsinic Acid (XVI)*.—5-Aminosalicylic acid hydrochloride (50 g.) was dissolved in water (400 c.c.) and concentrated hydrochloric acid (55 c.c.) and diazotised by the addition of 10% sodium nitrite solution (210 c.c.) in the presence of ice chippings (500 g.). A solution of arsenious oxide (30 g.) in 4% aqueous sodium hydroxide (400 c.c.) was then slowly added to the resultant suspension of diazo-oxide, and after the subsequent addition of freshly precipitated copper (prepared from 50 g. of copper sulphate)

the mixture was slowly made faintly alkaline to litmus paper. After 12 hours and readjustment of the reaction from time to time, the liquid was treated with 40% sodium hydroxide solution to decompose complex copper salts and filtered. The filtrate was made acid to Congo-paper and evaporated under reduced pressure at 50° to 400 c.c. A mass of cream-coloured needles of salicylic acid 5-arsinic acid (24 g.) separated on cooling and a further amount (8 g.) was obtained by saturating the mother-liquor with sodium chloride and keeping it at 0°. The total product was dissolved in 2*N*-ammonia, treated with norit, and precipitated at 90° with hydrochloric acid and finally recrystallised from boiling 50% aqueous methyl alcohol. The acid showed all the properties assigned to it by Kahn and Benda (*Ber.*, 1908, **41**, 3863), who prepared it from *o*-toluidine (see also O. and R. Adler, *Ber.*, 1908, **41**, 933; Karrer, *ibid.*, 1915, **48**, 1061). So prepared, it crystallises with one molecule of water of crystallisation (Found in air-dried material: loss at 100°, 6.9; As, 26.7. Calc. for  $C_7H_7O_6As \cdot H_2O$ :  $H_2O$ , 6.4; As, 26.8%).

*Salicylic Acid 5-Arsinous Acid* (XX).—A solution of the above arsinic acid (2 g.) in water (10 c.c.) and concentrated hydrochloric acid (1 c.c.) was saturated with sulphur dioxide in presence of a trace of potassium iodide. After 24 hours, a cream-coloured powder of *salicylic acid 5-arsinous acid* (1.6 g.) separated (Found: As, 30.2.  $C_7H_7O_5As$  requires As, 30.5%).

*Salicylic Acid 5-Dichloroarsine* (XIX).—Salicylic acid 5-arsinic acid (7 g.) was dissolved in a boiling mixture of ethyl alcohol (7 c.c.), water (15 c.c.), and concentrated hydrochloric acid (40 c.c.), a small crystal of potassium iodide added, and the solution saturated with sulphur dioxide. The oil which separated at first rapidly solidified to a mass of compact prisms. After 4 hours, it was collected (6.8 g.) and recrystallised by dissolution in the minimum volume of boiling 50% aqueous methyl alcohol, followed by the addition of concentrated hydrochloric acid until a turbidity was produced (Found: As, 26.4.  $C_7H_5O_5Cl_2As$  requires As, 26.5%).

*Methyl Salicylate-5-arsinic Acid* (XVII).—The esterification of salicylic acid 5-arsinic acid by the Fischer-Speier method proceeds very slowly in 1.5% methyl-alcoholic sulphuric acid; if a 10% methyl-alcoholic solution of salicylic acid 5-arsinic acid containing 10% sulphuric acid is used, the methyl ester may be obtained in 70% yield after 3 hours' refluxing. The ester is most conveniently isolated by removing nearly all the methyl alcohol under reduced pressure at room temperature, followed by addition of water (equal in volume to the residue). *Methyl salicylate-5-arsinic acid*, m. p. 208° (efferv.), crystallises from 4 parts of boiling 50% methyl alcohol in small prisms (Found: MeO, 9.4; As, 27.3.  $C_8H_9O_6As$  requires

MeO, 11.2; As, 27.2%). If the solution is refluxed for a longer period or if more sulphuric acid is used, some of the arsenic acid decomposes with formation of arsenious oxide. Saturation of a boiling 10% methyl-alcoholic solution of the arsenic acid (7 g.) with dry hydrogen chloride, followed by removal of most of the methyl alcohol, causes crystals of methyl salicylate-5-dichloroarsine (2 g.) to separate. Addition of water (20 c.c.) to the filtrate from this product gives methyl salicylate-5-arsinic acid (5 g.).

*Methyl Salicylate-5-dichloroarsine* (XVIII).—(i) *From salicylic acid 5-arsinous acid*. The arsenious acid (10 g.), dissolved in anhydrous methyl alcohol (15 c.c.), was heated with dry hydrogen chloride at 10° until saturated. After 4 hours, methyl salicylate 5-dichloroarsine (10 g.) had separated and was crystallised from boiling benzene. (ii) *From salicylic acid 5-dichloroarsine*. Salicylic acid 5-dichloroarsine (5.1 g.) was dissolved in dry methyl alcohol (6 c.c.) and saturated with hydrogen chloride at 10°. The mass of crystals was removed after 2 hours and a further amount was obtained by adding concentrated hydrochloric acid (5 c.c.) to the filtrate. The total yield was 4.6 g. When crystallised from boiling benzene, *methyl salicylate-5-dichloroarsine*, m. p. 168°, was obtained in small prisms. It proved to be identical both with that obtained from salicylic acid 5-arsinous acid and with that obtained in the treatment of salicylic acid 5-arsinic acid with methyl-alcoholic hydrogen chloride (Found: MeO, 8.2; Cl, 23.8; As, 25.7.  $C_8H_7O_3Cl_2As$  requires MeO, 10.5; Cl, 23.9; As, 25.3%). This substance is soluble in sodium hydroxide, but in sodium hydrogen carbonate solution a white solid (methyl salicylate-5-arsinous acid) remains after the effervescence has ceased. When it is treated with ammonia at room temperature, extensive decomposition takes place.

Methyl salicylate-5-arsinic acid may be conveniently prepared from this dichloroarsine; it is essential, however, to keep the reaction mixture at 0° during the manipulations, otherwise most of the product consists of the carboxylic acid. The dichloroarsine (5.1 g.) was ground under saturated sodium hydrogen carbonate solution (10 c.c.), removed, suspended in a further quantity of this reagent (20 c.c.), and slowly treated with 30% hydrogen peroxide (2.2 g.) in water (10 c.c.). After being kept at 0° for 1 hour, the liquid was made acid, and the precipitated methyl salicylate-5-arsinic acid collected (3.1 g.).

*Salicylamide-5-arsinic Acid* (XIV).—A suspension of the finely ground methyl ester (6 g.) in methyl alcohol (15 c.c.) and aqueous ammonia (20 c.c., *d* 0.88) was heated in a sealed tube at 100° for 5 hours. The free ammonia and part of the solvents were removed under reduced pressure at 50° and the residual solution was made

faintly acid to Congo-paper. Large rhombs separated slowly on keeping. They were purified by dissolving them in the smallest amount of 2*N*-ammonia, adjusting the reaction to faint acidity to litmus, and treating the solution with charcoal. When it was made faintly acid to Congo-paper, *salicylamide-5-arsinic acid*, unmelted at 300°, separated (yield, 3.9 g.) (Found: N, 5.6.  $C_7H_8O_5NaS$  requires N, 5.4%). This amide is much more soluble in dilute hydrochloric acid than in water.

*m-Xylyl-4-arsinic Acid*.—This acid has been previously prepared by Michaelis from tri-*m*-xylylarsine (*Annalen*, 1902, 320, 333). After numerous trials the following conditions were found satisfactory for its preparation from *m*-4-xylidine. A solution of *m*-xylidine (40.5 g.) in concentrated hydrochloric acid (60 c.c.) and water (150 c.c.) was diazotised with 10% sodium nitrite (210 c.c.) in the presence of ice-chippings (450 g.). This solution was run into another consisting of arsenious oxide (45 g.) and 50% aqueous sodium hydroxide (160 c.c.) in water (750 c.c.) which had just previously been heated to 90°, and 20% aqueous copper sulphate (20 c.c.) added. The mixing was complete in 15 minutes and after an hour the liquid was made weakly acid to litmus paper and filtered from tar. Evaporation of the filtrate (to 700 c.c.), followed by acidification to Congo-paper, gave cream-coloured *m*-xylyl-4-arsinic acid (42.6 g.) which was sufficiently pure for oxidation. One crystallisation from 20% aqueous alcohol gave fine elongated leaflets, m. p. 210—212° (Michaelis gives m. p. 210°).

*isoPhthalic Acid 4-Arsinic Acid* (XXI).—This acid was also obtained by Michaelis (*loc. cit.*) by oxidation of the corresponding xylylarsinic acid with permanganate. The large volumes used by Michaelis can be avoided by the following process (compare Maschmann, *Ber.*, 1924, 57, 1763). A vigorously stirred solution of *m*-xylyl-4-arsinic acid (23 g.) in 0.2*N*-sodium hydroxide (500 c.c.; 1 mol.) was treated with small amounts of finely powdered permanganate (35 g.) at 70—75° over a period of several hours. The solution was finally boiled and any excess of permanganate destroyed by alcohol. After filtration the press-cake was re-extracted twice by suspending it in 500 c.c. of 0.2*N*-sodium hydroxide and bringing the mixture to the boiling point with stirring. (The acid is retained tenaciously by the manganese oxides.) The combined filtrates were acidified to Congo-paper and concentrated. The total yield of acid was 73.4% of the theoretical. The purity of the successive crops obtained can be controlled by titration under standard conditions in comparison with a sample of the pure acid.

*Action of Thionyl Chloride on isoPhthalic Acid 4-Arsinic Acid*.—The acid (5.8 g.) was gently boiled for 3½ hours with excess (47 g.)

of freshly distilled thionyl chloride. The residue obtained on removal of the solvent was dissolved in dry toluene and added portionwise to 140 c.c. of chilled 2*N*-ammonia in a bottle and vigorously shaken. The toluene was removed under reduced pressure and perhydrol (2.3 g.) was added to the clear aqueous solution. On concentration to a small volume and acidification, *isophthalamic acid 6-arsinic acid* (XV) separated (yield, 4.45 g.). For analysis it was recrystallised from 30 volumes of boiling water, separating in well-formed glassy prisms (Found: loss at 100°, 5.9, 6.2.  $C_8H_8O_6NAs.H_2O$  requires  $H_2O$ , 5.9%. Found in anhydrous acid: N, 4.9; As, 26.1.  $C_8H_8O_6NAs$  requires N, 4.85; As, 25.9%). This acid also crystallises in short needles. Both forms are unmelted at 300°.

*Action of Phosphorus Pentachloride on isoPhthalic Acid 4-Arsinic Acid.*—(a) *With 5.5 molecular proportions of phosphorus pentachloride.* Finely powdered *isophthalic acid 4-arsinic acid* (5.8 g.) was mixed with 22.9 g. of phosphorus pentachloride and after the vigorous reaction had subsided, during which chlorine was evolved, the product was heated in an oil-bath at 110° (external temperature) for 3 hours. The phosphorus oxychloride was distilled off under reduced pressure and the residue, dissolved in sodium-dried toluene, was added portionwise to 160 c.c. of chilled 2*N*-ammonia with vigorous shaking. The toluene was separated, and the aqueous layer extracted once more with benzene. The combined extracts, evaporated to dryness, left 0.05 g. of 3:4-dichlorobenzamide, m. p. 163° (see below, section b). The aqueous layer was evaporated at 50° to a small volume and deposited 0.8 g. of crude 4-chloro-*isophthalamide* (XXII), m. p. 223—226°. This amide is soluble in 17 parts of boiling water and crystallises in needles, elongated leaflets, and in square plates, m. p. 232—233° (Found: N, 14.2.  $C_8H_7O_2N_2Cl$  requires N, 14.1%). On hydrolysis with boiling *N*-potassium hydroxide solution it gave 4-chloro-*isophthalic acid*. This acid is very sparingly soluble in boiling water, requiring 130 parts for solution. It crystallises therefrom in fine needles, m. p. 290—292° (Found: equiv., 104. Calc., 100.3). In its properties it accords best with those given by Ullmann and Uzbachian (*Ber.*, 1903, 36, 1799).

The mother-liquor of the chloro-*isophthalamide* was made distinctly alkaline by the addition of sodium hydroxide and perhydrol (2.3 g.) was added. On acidification the half-amide of *isophthalic acid 4-arsinic acid* (3.25 g.) separated, identical with that obtained by the use of thionyl chloride.

(b) *With 6.5 molecular proportions of phosphorus pentachloride.* The acid (10.75 g.) was mixed with powdered phosphorus penta-

chloride (50 g.) in a small distillation flask, and the chlorine and phosphorus oxychloride produced were allowed to distil off. The flask was then immersed in an oil-bath kept at 150–160° for 5 hours. Most of the phosphorus oxychloride had distilled off at the end of the first hour's heating. The product was worked up similarly to the foregoing. The benzene-toluene extract on evaporation deposited 0.25 g. of crude 3 : 4-dichlorobenzamide, m. p. 140–156°, which on recrystallisation from 15 c.c. of water separated in large leaflets, m. p. 166–168°. Of this, 0.05 g. was hydrolysed by boiling *N*-potassium hydroxide (1.25 c.c.) and on acidification gave 3 : 4-dichlorobenzoic acid as a felt of microscopic crystals. It was recrystallised from a large volume of boiling water and separated in microscopic pointed leaflets, m. p. 211–212°. The amount available was insufficient for complete analysis, but 0.0372 g. on titration required 2.05 c.c. of *N*/10-alkali, whereas the calculated figure is 1.95 c.c.

The aqueous layer, freed from ammonia and toluene by distillation at 40°, gave 4-chloroisophthalamide (6.0 g.), m. p. 223–227°; the mother-liquor on concentration gave a further 0.65 g. of the same substance. No other product could be found.

*Methyl isoPhthalate-4-arsinous Acid.*—*iso*Phthalic acid 4-arsinic acid (20 g.) was suspended in 150 c.c. of dry purified methyl alcohol (wood spirit), and a current of dry hydrogen chloride passed till saturation was complete at 0°. The clear dark brown solution was then heated for 5 hours under reflux, the passage of dry hydrogen chloride being continued. During this process a dark lower layer containing methyl *isophthalate-4-dichloroarsine* separated. The major portion of the supernatant layer was removed by heating under reduced pressure, and the residue poured into 250 c.c. of saturated sodium hydrogen carbonate solution cooled below 0°. The insoluble grey rubbery mass gradually disintegrated and solidified. It consisted of almost pure *methyl isophthalate-4-arsinous acid* (yield, 19 g.) (Found : MeO, 15.1; As, 24.6.  $C_{10}H_{11}O_6As$  requires MeO, 20.5; As, 24.8%). Treatment of this ester with aqueous methyl-alcoholic ammonia at 100° led to extensive decomposition.

*Methyl isoPhthalate-4-arsinic Acid.*—The arsinous acid (19 g.) was suspended in water (50 c.c.) at 0° and treated with sodium hydrogen carbonate (2.2 mols.) and 30% hydrogen peroxide (1.1 mols.). Rapid effervescence occurred and when solution was complete acidification gave microscopic square plates of *methyl isophthalate-4-arsinic acid* (20.5 g.) (Found : As, 23.6.  $C_{10}H_{11}O_7As$  requires As, 23.6%). This acid is fairly readily soluble in hot water and crystallises therefrom in long needles, which effervesce at 196–197° and then rapidly resolidify. The plate form of crystal

effervesces at  $185^{\circ}$  and then rapidly resolidifies (anhydride formation).

*Methyl isoPhthalate 4-Arsinetetrachloride.*—The dicarboxy-acid (5 g.) was suspended in 35 c.c. of synthetic methyl alcohol at  $-5^{\circ}$ , and the liquid saturated with dry hydrogen chloride. The acid dissolved after 1 hour and after a few more hours pale yellow needles began to separate. When separation was complete the solid was rapidly collected, washed with sodium-dried ether, and quickly dried in a vacuum. The *arsinetetrachloride* (2.5 g.) is highly hygroscopic and has m. p.  $110-115^{\circ}$  (efferv.) (Found: Cl, 31.7.  $C_{10}H_8O_4Cl_4As$  requires Cl, 34.6%). The low chlorine content indicates slight hydrolysis to the oxychloride, since the product was free from trivalent arsenic compounds. When added to saturated sodium hydrogen carbonate solution at  $0^{\circ}$ , it rapidly dissolved and on acidification gave methyl *isophthalate-4-arsinic acid*, identical with the product described above. Characteristic is its separation in microscopic plates on acidification but in needles when recrystallised from water.

*Action of Ammonia on Methyl isoPhthalate-4-arsinic Acid.*—Methyl *isophthalate-4-arsinic acid* (28.4 g. of the plate form) was added to 284 c.c. of ammonia ( $d$  0.88) previously cooled to  $-5^{\circ}$ . The mixture was kept below  $0^{\circ}$  for 14 days, during which the gelatinous ammonium salt which originally separated had disappeared with formation of a loose powder. The ammonia was removed as far as possible at room temperature and then, with some concentration of the solution, at  $45^{\circ}$ . On strong acidification to Congo-paper, a large crop of crystals separated, and on concentration of the mother-liquor at  $50^{\circ}$  further crops were obtained, making 25.2 g. in all. This material was subjected to fractional crystallisation, the more sparingly soluble fractions (16.0 g.) consisting of *isophthalamic acid 6-arsinic acid* identical with that obtained previously. The more soluble fractions were further carefully fractionated, and the nitrogen content and titration equivalents determined. They consisted mainly of the above half-amide mixed with varying proportions of esters. There was no evidence for the presence of a diamide in any fraction.

If the original solution is not acidified strongly to Congo-paper, the product contains an *acid ammonium* salt of *isophthalamic acid 6-arsinic acid* which, being readily soluble in water, separates in the later fractions. It crystallises in fine silky needles (Found: N, 8.9.  $C_8H_{11}O_6N_2As$  requires N, 9.1%). The use of methyl-alcoholic ammonia at higher temperatures was no more successful.



*Derivatives of Sulphophenylarsinic Acid.*

*Benzenesulphonyl Chloride p-Dichloroarsine* (XXV).—*p*-Sulphophenylarsinic acid (13.2 g., prepared as described by Hewitt, King, and Murch, J., 1926, 1369) was suspended in carbon tetrachloride (132 c.c.), and phosphorus pentachloride (58 g.; 6 mols.) added. On warming, hydrogen chloride and chlorine were rapidly evolved. After 1.5 hours' refluxing, the substances volatile at 50°/20 mm. were removed and the residue was poured into a mixture (200 c.c.) of equal volumes of concentrated hydrochloric acid and water. The precipitated oil rapidly solidified (13.1 g.) and when dry was crystallised from benzene. *Benzenesulphonyl chloride p-dichloroarsine* separated in stout rhombs (Found: Cl, 33.2.  $C_6H_4O_2Cl_3SAs$  requires Cl, 33.1%).

*Benzenesulphonyl Chloride p-Arsenious Oxide*.—The corresponding dichloroarsine (1 g.) was ground with water and kept for 12 hours. The amorphous product was pure *benzenesulphonyl chloride p-arsenious oxide* (0.8 g.), almost insoluble in water or organic solvents (Found: Cl, 13.5.  $C_6H_4O_3ClSAs$  requires Cl, 13.3%). The aqueous filtrate contained a small quantity of deliquescent *p-sulphophenylarsinous acid*, which may be more readily prepared by boiling either of the sulphonyl chloride compounds with water and evaporating the resultant solution repeatedly to dryness with water.

*Benzenesulphonamide-p-arsenious Oxide* (XXVI).—Benzene-sulphonyl chloride *p-dichloroarsine* (5.8 g.), dissolved in benzene (15 c.c.), was slowly added to 2*N*-aqueous ammonia with vigorous shaking. Towards the end of the reaction a white solid separated (2 g.), and a further precipitate (2.6 g.) was obtained by removing the benzene and evaporating the aqueous solution (to 30 c.c.). The united crops were dissolved in hot sodium hydrogen carbonate solution and precipitated with acid. *Benzenesulphonamide-p-arsenious oxide* is an amorphous substance which is much more soluble in water than the corresponding benzamide compound (Found: As, 28.2.  $C_6H_6O_3NSAs$  requires As, 28.3%). On treatment with hydrochloric acid it is readily converted into *benzenesulphonamide-p-dichloroarsine*. For the preparation of this substance sufficient ethyl alcohol was added to a suspension of the arsenious oxide (1 g.) in water to give a clear solution on boiling, and concentrated hydrochloric acid (15 c.c.) slowly added. On cooling, a mass of fine needles (0.82 g.) separated, m. p. 176–178° (Found: Cl, 23.3; As, 25.0.  $C_6H_6O_2NCl_2SAs$  requires Cl, 23.5; As, 24.8%).

*Benzenesulphonamide-p-arsinic Acid* (XXVII).—A suspension of benzenesulphonamide-*p-arsenious oxide* (8.7 g.) in water (30 c.c.) was mixed with a solution of 30% hydrogen peroxide (4.4 g.) in

water (20 c.c.). The mixture became hot, most of the solid dissolved, and the undissolved portion became crystalline. The reaction was completed by heating until a clear solution was obtained. On allowing the liquid to cool, stout rhombic tablets of *benzenesulphonamide-p-arsinic acid* separated. They were recrystallised from boiling water (60 c.c.) and gave 6.7 g. of pure amide (Found: N, 4.8.  $C_6H_8O_5NSAs$  requires N, 5.0%).

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### XC.—*The Heats of Association of Acetic and Heptioic Acids in the Vapour State.*

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THE work of Ramsay and Young on the vapour pressures and vapour densities of acetic acid (*Sci. Proc. Roy. Dublin Soc.*, 1910, **12**, 374; *J.*, 1886, **49**, 790) showed that this substance was associated in the vapour state, and that the degree of association decreased with increase in temperature. It is possible to calculate an approximate value for the heat of association from their data by means of the equation  $d \log K_c/dT = -Q_v/RT^2$ . We have now repeated this work and our results are in better concordance with one another than are those of the above authors; the values of  $Q_v$  found from the two investigations are 12,420 and 13,790 cal. per g.-mol., respectively.

The primary object of the present investigation was to determine  $Q_v$  for acids with longer chains, with a view to obtain evidence as to the nature of the linkage between the molecules of acids. The heat of vaporisation of acetic acid at 110° is less than one-half of  $Q_v$  (5,170 cal.; Young), which indicates that the forces holding the molecules together are greater than those causing condensation from the vapour to the liquid state. If the attachment is by means of the two carboxyl groups to give double molecules, then  $Q_v$  should approach a practically constant value as the homologous series of monobasic acids is ascended, and it would be expected that this constant value would be reached when the length of chain exceeded five or six carbon atoms. If, on the other hand, the association occurs by linking through the methylene groups, then the heat of association should increase with increasing length of chain.

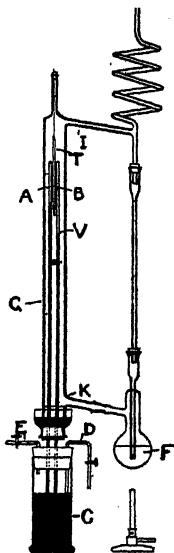
Accordingly, heptioic acid has been studied, and shown to be about 10% associated at its boiling point. A value for  $Q_v$  has been determined, viz., 7,050 cal. per g.-mol., but on account of the low

degree of association, this is much less accurate than that of acetic acid. Thus the heat of association decreases with increase in chain length, a result which is in accord with the view that linking occurs through the carboxyl groups, and not through the hydrocarbon chains, and that the residual affinity of the carboxyl group decreases with increasing chain length. Acids with shorter chains must, however, be investigated before this conclusion can be substantiated.

#### EXPERIMENTAL.

*Apparatus.*—The modified form of Ramsay and Young's apparatus used in the present series of experiments consists of two Pyrex-glass tubes A and B, about 90 cm. long, standing in a gas-jar C containing mercury (Fig. 1) and bound together by copper wire, a short asbestos pad being inserted to keep them vertical. C is closed by a rubber bung which carries two other tubes, D and E. D is bent twice at right angles and serves to remove the excess mercury introduced during the setting up of the apparatus. E is connected by means of a piece of glass tubing (fitted with a tap) to a water pump.

FIG. 1.



A and B were heated by the vapour from liquid boiling in the flask F, which is connected by a ground-glass joint to the cylindrical glass jacket G. The top of G has a side tube I connecting with a glass spiral open to the air and a tube leading back to the bottom of F. A spiral of nichrome wire is wound round the tube G, which is heated by an electric current. The wire is wound on strips of asbestos so placed as to leave a window in the back and front of the tube. G rests in a glass trough containing mercury, which consists of the top of a wide-mouthed bottle cut off near the top, the mouth being closed by a rubber bung through which A and B pass.

The whole apparatus from I to K is enclosed in an asbestos-lined box, to protect it from draughts, which has glass windows back and front, the front window consisting of a calibrated glass scale. A fine mark was etched near each end of A, and the volume between these two marks determined for each cm. length of tube.

The thermometers used were either standard or had been checked against standards, at or near the temperatures of the vapours used in the tube G.

*Materials.*—Kahlbaum's acetic acid was used, and its purity was determined by titration with *N*/10-sodium hydroxide which had

been standardised against pure crystallised succinic acid. The acid was found to be 99.2% pure, and was then partly (about two-thirds) frozen, and the liquid separated. This process was repeated, and the solidified acid used for the experiment. The weights of acid used were approximately 0.1, 0.07, and 0.08 g. in three series of experiments.

*Preparation of Tubes for Vapour-density Determination.*—The tubes A and B were left for 24 hours full of freshly made chromic acid solution, and then repeatedly rinsed with distilled water and dried by a current of hot air. Dry mercury was poured into them to a depth of 5–6 cm. at a time, and each portion was boiled to expel any air trapped between the mercury and the walls. The two tubes (which had previously been pushed through the two bungs) were inserted in the gas-jar full of mercury and a weighed quantity of acetic acid contained in a small Victor Meyer bottle was introduced into the calibrated tube. The bung was then pushed firmly into the gas-jar C, the excess mercury being run out through the side tube D. The gas-jar was then anchored by copper wire to the sides of the tray in which the apparatus stood and a forked support attached to a heavy retort-stand was pushed under the bung closing the mercury seal. The tube E was connected to the pump and the apparatus was made gas-tight by means of melted gutta-percha at the glass-rubber connexion.

The jacket and flasks were then fitted on, and the electrical heating was adjusted so that the temperature was about 10–20° below the boiling point of the jacketing liquid. The liquid in the flask was then boiled until steady circulation of the vapour occurred. The temperature was measured by means of three standardised thermometers suspended at intervals between the two experimental tubes.

The pressure was obtained from the difference between the levels of the mercury in the two tubes. Since the temperature of the two tubes was the same, the vapour pressure of mercury and the density of the liquid mercury in the tubes were identical. The difference in level, multiplied by the density of mercury, therefore gave the pressure of the vapour of acetic acid.

To read the mercury level, a diffuse light was placed behind the apparatus so that the meniscus showed black against it. The telescope was first adjusted so that the cross-wires touched the top of the meniscus, and then readjusted until the glass scale was in focus, whereupon the scale reading was taken, decimals of a millimetre being determined by means of a vernier on the cathetometer. The volume was calculated from the height of mercury in the experimental tube and allowance was made for the volume of the

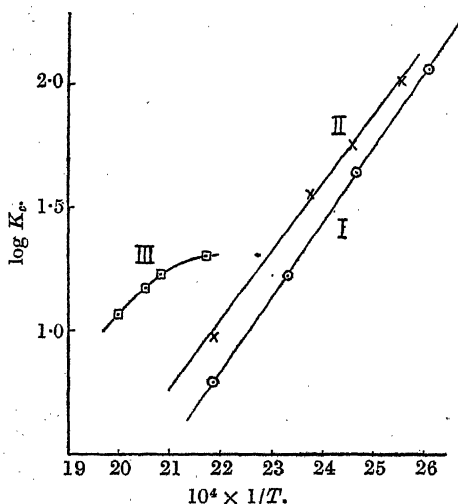
Victor Meyer bottle. The volume correction for expansion of the glass tube is negligible for the range of temperatures used.

From these measurements the ratio of the apparent to the real molecular weight was determined by the formula

$$R = \frac{w}{M} \cdot \frac{22,400}{v} \cdot \frac{T}{273} \cdot \frac{760}{p} \cdot \frac{13.6}{\delta},$$

where  $w$  = weight of acid introduced,  $M$  = molecular weight of acid,  $v$  = volume (in c.c.),  $p$  = observed pressure (in mm.),  $T$  = absolute temperature of experiment, and  $\delta$  = density of mercury at  $T^\circ$  Abs.

FIG. 2.



I. *Acetic acid (authors).* II. *Acetic acid (Young).*  
III. *Heptoic acid.*

Assuming that the association of acetic acid is due to the reaction,  $2\text{CH}_3\cdot\text{CO}_2\text{H} \rightleftharpoons (\text{CH}_3\cdot\text{CO}_2\text{H})_2$ , we have for the equilibrium constant,  $K_p = p_{A_2}/p_A^2$ , where  $p_{A_2}$  is the partial pressure due to double molecules and  $p_A$  that due to single molecules; therefore  $K_p = (R - 1)/p(2 - R)^2$ .

In Table I are collected the data for acetic acid (under the symbols defined above) together with the average value of  $K_c$  calculated from  $K_c = K_p \cdot 760 \cdot T \cdot 22.4/273$ .

The plot of  $\log K_c$  both for our results and for Young's (J., 1886, 49, 790) is given in Fig. 2, and it will be seen that, although both sets lie on straight lines, the two curves are not coincident.

The average values of  $K_c$  are employed in the calculation of the

heat of reaction at constant volume in the usual way and give the results shown in Table II.

TABLE I.  
*Data for acetic acid.*

No. of expts.	Series.	v.	p.	$T - 273^\circ$ .	R.	$K_p \times 10^6$ .	Mean $K_c$ .
1	1	67-255	499-980	131-03°	1-380	197	44-16
1	1	67-469	499-868	130-0	1-379	197	
1	2	60-575	425-724	132	1-320	163	
1	2	69-561	374-403	132	1-307	171	
1	2	70-785	369-460	132	1-301	167	
1	2	60-774	424-661	132	1-319	162	
4	2	61-265	416-139	131-9	1-335	181	
2	2	63-642	402-825	131-9	1-328	180	
1	3	57-632	463-490	131-93	1-339	167	
1	3	58-004	460-481	131-8	1-339	168	
4	3	57-979	460-210	131-9	1-341	170	
1	1	74-292	550-836	154-9	1-209	64-2	16-86
3	2	64-224	475-852	155-73	1-185	58-5	
2	2	66-385	458-374	155-73	1-190	63-2	
2	2	68-199	448-378	155-73	1-184	61-8	
4	2	63-992	473-474	155-73	1-195	63-7	
4	3	62-438	505-594	156-05	1-206	64-8	
2	3	63-068	500-575	156-05	1-206	65-3	6-296
3	2	68-753	517-218	183-83	1-089	20-6	
5	2	69-131	512-222	183-83	1-093	21-0	
4	2	70-544	500-467	184-2	1-097	23-9	
4	2	69-012	511-432	183-8	1-097	23-2	
3	3	66-911	556-007	183-9	1-099	21-8	
2	3	66-900	553-190	183-9	1-099	22-2	
1	3	67-240	552-257	183-9	1-095	21-1	
1	1	66-741	554-844	183-9	1-098	21-8	
1	1	63-974	453-390	110-11	1-514	480	117-00
1	1	63-157	454-285	110-1	1-531	506	
1	1	63-688	453-659	110-1	1-520	496	
1	1	65-867	438-050	110-1	1-522	522	
3	2	71-227	306-000	110-5	1-444	469	
2	2	64-580	331-850	110	1-468	436	
2	2	55-373	379-600	110-8	1-499	524	

TABLE II.

$K_{c1}$ .	$K_{c2}$ .	$T_1$ .	$T_2$ .	$Q_c$ .
44-16	16-86	404-68	428-70	13,800
44-16	6-296	404-68	456-91	13,690
117-00	44-16	383-24	404-68	14,000
16-86	6-296	428-70	456-91	13,580
117-00	16-86	383-24	428-70	13,900
117-00	6-296	383-24	456-91	13,790
				Mean 13,790

X-Ray evidence shows that, in the solid state, the carboxyl groups of adjacent molecules of monobasic acids are attached to one another, and it is not unlikely that the molecules of acetic acid are attached in a similar manner in the vapour state. On this view, the heat of association of acetic acid would be the heat of association of carboxyl groups, and the high value of this heat may be ascribed

to an atomic rearrangement occurring between these groups on association.

*Determination of the Heat of Association for Heptioic Acid.*—The heptioic acid, obtained by repeated fractionation of a specimen from Kahlbaum, had been employed in a determination of heats of crystallisation, and melted at  $-7.5^{\circ}$ ; its purity was found by titration to be 98.79%.

The mode of heating the tube G was modified slightly, since, for the higher temperatures, the fall of temperature along the tube was about  $5^{\circ}$  when the vapour was distilling through it. The wiring was therefore readjusted until the electrical heating by itself gave a fall of only  $6^{\circ}$ ; with the circulating vapour, this gave a satisfactorily constant temperature with a fall of about  $1^{\circ}$ , and the average temperature was taken. The three jacketing vapours used were aniline, benzyl alcohol, and methyl salicylate. The weights of acid used were 0.06 and 0.03 g. approximately. Table III gives the results obtained at four temperatures. Partly owing to the difficulty of maintaining constant temperatures at  $200^{\circ}$  and above, and partly owing to the low degree of association of heptioic acid, the values of  $K_p$  are much less concordant than those obtained for acetic acid; and the corresponding values of  $Q_v$  (Table IV) do not

TABLE III.

No. of expts.	Series.	<i>v.</i>	<i>p.</i>	<i>T</i> — $273^{\circ}$ .	<i>R.</i>	$K_p \times 10$	Mean <i>K<sub>c</sub></i> .
3	1	47.838	292.626	230.5°	1.084	350	11.59
6	1	46.861	293.936	227	1.093	384	
1	2	39.163	203.481	225.5	1.067	379	
2	2	53.974	136.330	213.75	1.063	525	14.93
2	2	37.733	192.684	213.75	1.076	459	
2	1	43.554	292.806	206.3	1.130	587	
2	1	51.840	252.525	206.3	1.098	479	17.06
2	1	57.739	226.530	206.3	1.099	541	
2	1	43.560	292.659	206.3	1.128	576	
2	2	41.851	168.673	207.12	1.091	650	
2	2	52.255	137.391	207.8	1.074	629	
2	2	36.508	195.660	210.5	1.084	527	20.17
2	1	53.189	227.199	186.2	1.136	804	
2	1	62.637	197.001	185.2	1.101	604	
2	1	64.352	189.424	185.2	1.124	851	
2	2	34.902	192.599	187.75	1.096	612	
2	2	57.963	118.746	187.77	1.071	687	
2	2	34.964	193.021	191.00	1.100	640	

TABLE IV.

$K_a$ .	$K_{ca}$ .	$T_1$ .	$T_2$ .	$Q_v$ .
17.06	11.59	480.23	500.66	9,030
14.93	11.59	486.75	500.66	8,820
17.06	14.93	480.23	486.75	9,470
20.17	11.59	460.19	500.66	6,260
20.17	17.06	460.19	480.23	3,670
20.17	14.93	460.19	486.75	5,040

possess much value by themselves. Nevertheless, the results indicate that the heat of association of heptoic acid is decidedly lower than that of acetic acid. An investigation into the behaviour of acids of intermediate chain length would appear desirable.

*Summary.*

Acetic and heptoic acids have been shown to be associated in the vapour state and the heats of association have been calculated. For acetic acid,  $Q_v = 13,790$  cal. per g.-mol. over the temperature range  $110-184^\circ$ . For heptoic acid,  $Q_v$  appears to vary with temperature; the average value between  $185^\circ$  and  $230^\circ$  is  $7,050$  cal. per g.-mol. Since the heat of evaporation of acetic acid is only  $5,570$  cal. per g.-mol., it is concluded that the double molecules are held together by forces analogous to those of chemical combination.

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## XCI.—A Simple Method for the Preparation of Maleic Anhydride.

By FREDERICK ALFRED MASON.

MALEIC acid can now be obtained cheaply and conveniently on a commercial scale by the catalytic oxidation of benzene, but the preparation of maleic anhydride by existing methods involves the use of an expensive dehydrating agent such as acetyl chloride or phosphoric oxide (compare Anschütz, *Ber.*, 1879, **12**, 2281; 1881, **14**, 2789; 1882, **15**, 641; Perkin, *Ber.*, 1881, **14**, 2547; 1882, **15**, 1073; Fittig, *Annalen*, 1877, **188**, 87; Volhardt, *ibid.*, 1892, **268**, 255; Tanatar, *ibid.*, 1893, **273**, 32; Van der Riet, *ibid.*, 1894, **280**, 216). The anhydride cannot be prepared by heating maleic acid just above its melting point (Pelouze, *Ann. Chim.*, 1834, **11**, 266), at  $130^\circ$  in a sealed tube (Skraup, *Monatsh.*, 1893, **14**, 500), at  $190^\circ$  (Tanatar, *loc. cit.*), or with water in a sealed tube (Skraup, *Monatsh.*, 1891, **12**, 107), the chief or sole product being fumaric acid in all cases; neither can it be prepared by distilling maleic acid rapidly in small quantities, since, according to Pelouze, the anhydride and the water in the distillate at once regenerate maleic acid.

It has now been found that the anhydride may be obtained from the acid in excellent yield by distilling the latter with a neutral high-boiling solvent such as xylene or, better, tetrachloroethane. The water formed distills at once with the solvent and as soon as all the water is removed the residue is fractionated under reduced



pressure; the anhydride then distils in a pure form, only about 10% of the acid remaining behind as fumaric acid.

#### EXPERIMENTAL.

A mixture of 100 c.c. of tetrachloroethane and 100 g. of commercial maleic acid was heated, preferably in an oil bath, until 90 c.c. of distillate had been collected, consisting approximately of 75 c.c. of tetrachloroethane and 15 c.c. of water (theory requires 15.5 c.c.), the temperature rising from 120° to 150° as indicated by a thermometer placed in the neck of the flask. The residue was then distilled until the thermometer indicated 190° (b. p. of anhydride 197—199°), the receiver changed, and the residual anhydride distilled under reduced pressure, boiling at 82—84°/15 mm. (reduced pressure is desirable but not essential): 70 g. of anhydride were collected, and the middle fraction on refractionation gave a further 5.5 g., the total yield being 75.5 g. or 89.5% of the theoretical. The residue (8.5 g.) of fumaric acid in the flask was removed with alcohol and still contained a small amount of anhydride.

Similar results were obtained when xylene was used as the solvent, but the water came over much more slowly; for instance, the distillate from a mixture of 50 g. of maleic acid and 100 c.c. of xylene contained 2 c.c., 3 c.c., and 5.5 c.c. of water in 50 c.c., 70 c.c., and 80 c.c. respectively.

The anhydride so obtained has a boiling point of 197—199° (uncorr.) and a setting point of 52° (Fittig gives 196° and 60°). It is easily soluble in most organic solvents and crystallises well on cooling. On exposure to the air it absorbs moisture, re-forming maleic acid.

Attention must be directed to the fact that the vapour of the anhydride, although having no perceptible odour at the ordinary temperature, attacks the mucous membrane of the nose and after some time causes inflammation and a heavy catarrh of the nasal passages, the symptoms resembling those of a severe "common cold."

The experiments were carried out in the Organic Chemical Laboratories at Oxford and thanks are due to Imperial Chemical Industries Ltd. for permission to publish the results.

COLLEGE OF TECHNOLOGY,  
MANCHESTER.

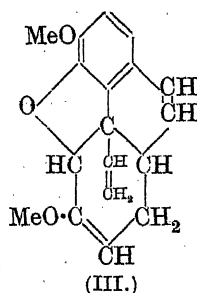
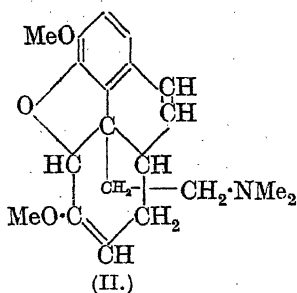
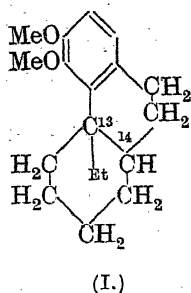
[Received, February 11th, 1930].

## XCII.—*Further Degradative Experiments in the Morphine Group.*

By ROBERT SIDNEY CAHN.

THE following experiments are a continuation of earlier work (J., 1926, 2562) which had as its object the preparation, with a view to later synthesis, of 3:4-dimethoxy-13-ethyloctahydrophenanthrene (I) from the natural alkaloids of the morphine group. They have had to be discontinued \* short of ultimate success and are here placed on record for reference.

The route chosen must give no opportunity for wandering of the ethanamine side chain from C13 to C14 or other positions (compare Schöpf and Bardowsky, *Annalen*, 1927, 458, 148), and it is therefore worth noting that both dihydrothebainone, the initial material of the previous experiments, and dihydrothebaine, that of this series, undoubtedly contain the ethanamine chain attached to C13 and that no wandering was possible under the conditions of the later reactions.



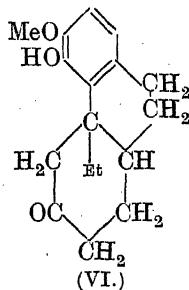
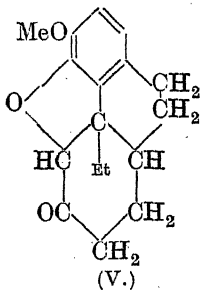
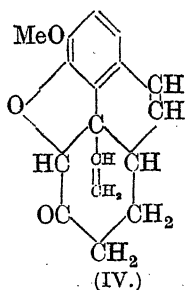
By heating the methiodide of dihydrothebainemethine † (II) with amyl-alcoholic potassium hydroxide, Freund and Speyer (*Ber.*, 1920, 53, 2250) obtained the vinyl compound (III) mixed with a red impurity. They gave the melting point of (III) as 150—151°, but their analyses showed the product to be impure. The formation of the red impurity has been confirmed, but the vinyl compound has been obtained pure by transforming the methiodide by means of silver oxide into the methohydroxide and refluxing this in isocamyl-alcoholic solution; the pure substance melts at 120—121°.

Hydrochloric acid readily hydrolyses 6-methoxy-13-vinyltetrahydromorphenol methyl ether (III) to 6-keto-13-vinylhexahydromorphenol methyl ether (IV), which absorbs two molecules of

\* The author's skin became sensitive to the catalytic reduction products of thebaine. (Cure: frequent bathing with very hot boracic solution.)

† For nomenclature, see J., 1926, 2564, footnote.

hydrogen in the presence of platinised charcoal to give 6-keto-13-ethyloctahydromorphenol methyl ether (V). The ether bridge in (V)



is reduced by aluminium amalgam and moist ether, yielding 6-keto-13-ethyloctahydromorphol 3-methyl ether (VI), which has been prepared by a different route by Wieland and Kotake (*Annalen*, 1925, 444, 87). Neither method gives a good yield, probably because of partial reduction of the keto-group. Attempts to proceed further with the small quantity of (VI) available were unsuccessful.

The methohydroxide of dihydrothebainemethine (II) on decomposing gives only 30% of the vinyl compound (III), and 50% of the methine formed by loss of methyl alcohol can be recovered. The latter reaction was found to occur almost exclusively with three bases in the previous investigation (Cahn, *loc. cit.*), but reaches only negligible proportions in other cases, *e.g.*, thebenol and thebenone. Notwithstanding certain apparent regularities, it seems impossible to foretell the course of the degradation of these complicated bases; for instance, hydroxydihydrocodeinonemethine, which is structurally intermediate between the examples mentioned above, may be compared with the base (II), giving 48% of trimethylamine, whereas the closely related dihydromethylhydroxydihydrothebainonemethine gives less than 10% (Freund and Speyer, *J. pr. Chem.*, 1916, 94, 135; Schöpf, *Annalen*, 1927, 452, 256). The contradictions do not appear capable of explanation along the lines of the theoretical views of Ingold and his collaborators (*J.*, 1927, 997; 1928, 3125). In particular are they noteworthy when the deduction is drawn that the elimination of methyl alcohol from substances of the type  $R-CH_2-CH_2-NMe_3OH$  reaches a limit of 25% when R is *n*-butyl, and the statement is made (*J.*, 1929, 2338) that there is no known instance of "a complete disappearance of the reaction leading to an olefin, a tertiary amine and water." The consideration that the many-branched nature of the morphine radicals should increase the elimination of methyl alcohol applies equally to all these bases.

## EXPERIMENTAL.

All the analyses recorded in this paper are microanalyses made by Dr. Ing. A. Schoeller of Berlin.

**6-Methoxy-13-vinyltetrahydromorphenol Methyl Ether (III).**—A hot solution of dihydrothebainemethine methiodide (14 g.) in methyl alcohol (350 c.c.) was poured on silver oxide (precipitated from 7 g. of silver nitrate and washed free from alkali with water and then three times with methyl alcohol), cooled at once, shaken mechanically for 30 minutes, and filtered. The solvent was removed by distillation, and a solution of the residual oily quaternary hydroxide in *isoamyl* alcohol (140 c.c.) refluxed for 5½ hours. After removal of the *amyl* alcohol in steam, an insoluble oil was obtained which readily solidified. It was collected and dissolved in hot glacial acetic acid, the solution poured into ether, and the whole shaken with water. On basification of the acid layer pure dihydrothebainemethine (4.8 g.; 50% of the theoretical quantity) was precipitated. From the ethereal layer, dried over calcium chloride and evaporated, the vinyl compound (III) was obtained as a solid residue (2.5 g.; yield, 30%): on crystallisation from alcohol or slightly diluted acetic acid it formed colourless plates, m. p. 120–121° (Found: C, 76.2; H, 6.5; MeO, 21.9. Calc. for  $C_{18}H_{18}O_3$ : C, 76.55; H, 6.4; 2MeO, 22.0%). The same substance was on one occasion obtained, mixed with small red prisms, by heating the quaternary hydroxide for 2 hours on the steam-bath and working up the product as above, but several attempts to repeat the experiment failed.

**6-Keto-13-vinylhexahydromorphenol Methyl Ether (IV).**—Concentrated hydrochloric acid (1.5 c.c.) and a solution of the dimethoxy-compound (III) (1.4 g.) in alcohol (14 c.c.) were heated together for 30 minutes on the water-bath and hot water was then added until a turbidity was produced. The ketone (IV) (1.36 g.), which was deposited on cooling, crystallised from alcohol in colourless elongated prisms, m. p. 149°.

**6-Keto-13-ethyloctahydromorphenol Methyl Ether (V).**—A solution of the substance (IV) (1.2 g.) in alcohol (120 c.c.), containing 1 g. of charcoal on which the palladium from 0.2 g. of palladous chloride had been precipitated, was stirred in the presence of hydrogen. Absorption ceased after 275 c.c. of hydrogen (all volumes are corrected to N.T.P.) had been absorbed in 3 minutes. In a blank experiment the same amount of catalyst in alcohol (120 c.c.) adsorbed 81 c.c. The effective absorption was therefore 194 c.c. (2 mols. = 191 c.c.). After the reduction the solution was filtered and concentrated to small bulk; on cooling, substance (V) (1.1 g.) was deposited in clusters of rods, m. p. 113° (Found: C, 74.9; H, 7.3.

$C_{17}H_{20}O_3$  requires C, 74.9; H, 7.4%). The *semicarbazone*, crystallised from a little alcohol, melted at  $191^\circ$  after previous sintering (Found: N, 12.75.  $C_{18}H_{23}O_3N_3$  requires N, 12.8%).

6-*Keto-13-ethylotahydromorphol 3-Methyl Ether* (VI).—Freshly amalgamated aluminium (8 g.) was added to a solution of the substance (V) (0.5 g.) in wet ether (50 c.c.) and drops of water were added occasionally with shaking during 16 hours. After filtration and evaporation of the solvent the substance (VI) was obtained as an oil which soon solidified; after two crystallisations from alcohol it formed long prisms, m. p.  $148-150^\circ$  (Wieland and Kotake, *loc. cit.*, give  $148-150^\circ$ ). The low yield (0.25 g. after one crystallisation) was doubtless due to partial reduction of the keto-group, for in a later experiment with a larger proportion of amalgam the oily product would not solidify. In attempts to eliminate the oxygen from ring III the crystalline material and the oily product were subjected to reduction by Clemmensen's method, but an uncrystallisable oil was obtained in both cases. These last oils did not yield well-defined products when refluxed in benzene solution with methyl sulphate or methyl iodide in the presence of potassium carbonate. An attempt to methylate the crystalline substance (VI) by methyl sulphate and sodium hydroxide solution also failed.

The author is indebted to the Department of Scientific and Industrial Research for a grant, by the aid of which the early part of this work was carried out.

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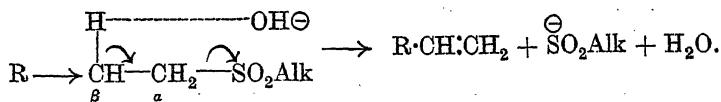
[Received, February 12th, 1930.]

### XCIII.—*Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part VII. A Generalised Form of the Olefinic Degradation of Sulphones.*

By GEOFFREY WILLIAM FENTON and CHRISTOPHER KELK INGOLD.

It was shown in Parts III and IV (J., 1928, 3127; 1929, 2338) that sulphones in the presence of concentrated potassium hydroxide solution undergo a degradation the mechanism of which is almost certainly identical in type with that which was applied in Parts I and II (J., 1927, 997; 1928, 3125) to the decomposition of quaternary ammonium hydroxides. The normal products of the degradation of sulphones are an olefin and a sulphinic acid, and the facility with which the reaction proceeds depends on the extent to

which the  $C_\gamma$ - $C_\omega$  part of the alkyl group ultimately eliminated as an olefin activates or de-activates the  $\beta$ -hydrogen atom attacked by hydroxide ion :



The straight arrow in the formula represents a de-activating effect, because electron-repulsion towards  $C_\beta$  must diminish the tendency of the  $\beta$ -hydrogen atom to separate in the kationic form; and in this connexion it was observed that, under the conditions used, the reaction became sluggish or failed altogether when R was a higher alkyl group than methyl. It also failed if there were two de-activating groups attached to  $C_\beta$ , even when these were only methyl groups. Although substitution at  $C_\alpha$  is not expected adversely to affect the degradation to any marked extent (the investigation of diisopropylsulphone supports this assumption), the reaction in the form in which we have described it is evidently far from being as general as the corresponding decomposition of quaternary ammonium hydroxides, and this is in agreement with the smaller electron-affinity of  $-\text{SO}_2\text{R}$  than of  $-\text{NR}_3^\oplus$  (see Parts III and IV).

Obviously, however, the sulphone degradation might be made general by the use of a more basic anion (*i.e.*, one with greater proton affinity) than hydroxide; and for this purpose the methoxide and ethoxide ions suggested themselves (Ingold and Shoppee, J., 1929, 447; Kon and Linstead, *ibid.*, p. 1269).

We find that the degradation can readily be generalised by the replacement of aqueous potassium hydroxide by alcoholic sodium ethoxide: all the sulphones which resisted the former reagent have been found to undergo the degradation in the presence of the latter.

No.	Sulphone.	Olefin.	KOH.	NaOEt.
1	Phenyl- $\beta$ -phenylethyl*	Styrene	*	*
2	Diethyl	Ethylene	*	*
3	Ethyl- <i>n</i> -propyl	"	*	—
4	Ethyl- <i>iso</i> amyl	"	*	—
5	Ethyl- <i>n</i> -octyl	"	*	—
6	Diisopropyl	Propylene	*	—
7	Di- <i>n</i> -propyl	"	*	*
8	Di- <i>n</i> -butyl	$\Delta^2$ - <i>n</i> -Butylene	Little action	*
9	Di- <i>n</i> -octyl	$\Delta^2$ - <i>n</i> -Octene	No action	*
10	Di- <i>iso</i> amyl	$\Delta^2$ - <i>iso</i> Amylene	"	*
11	Diisobutyl	<i>iso</i> Butylene	"	*

\* With potassium hydroxide the products were styrene, benzene, and sulphur dioxide, but when sodium ethoxide was used the benzenesulphinic acid formed was isolated as such. In all the other cases the sulphinic acid was obtained with either reagent.

The above is a tabular summary of the observations recorded

in Parts III and IV and in this paper. The examples studied are arranged in order of the theoretically anticipated inhibition to the elimination of the olefin formed. A star indicates that degradation by the reagent indicated has been observed, and a line that the corresponding experiment was not tried.

#### EXPERIMENTAL.

*Preliminary Experiments.*—Di-*n*-octylsulphone (Part III) was used because the liquid olefin *n*-octene could scarcely be confused with any unsaturated substance which might arise from the sodium ethoxide. The sulphone (4 parts), freshly prepared sodium ethoxide (10 parts), and alcohol (1.5 parts) were heated in a metal bath and the products were passed through water and bromine and into a eudiometer. Reaction occurred at just below 200° (bath temperature) and an oily product, but no gas, was evolved. The liquid product was identified by its b. p. 122—123°, and by conversion into its dibromide, as  $\Delta^a$ -*n*-octene. In a similar experiment the bath temperature was carried to 300° after the subsidence of the original reaction; and at this temperature both saturated and unsaturated gases were evolved. The unsaturated gas was represented by a small amount of oil which was obtained after destruction of the excess of bromine in the bromine trap. The gas collected in the eudiometer contained oxygen, nitrogen (which was used for sweeping), and hydrogen, but no hydrocarbons. The *n*-octene obtained in this experiment (yield, 50%; b. p. 120—125°) gave, on ozonolysis, formaldehyde as volatile product and an oil having the odour of heptaldehyde. We conclude that the gaseous products evolved at 300° come from the sodium ethoxide and that the  $\Delta^a$ -*n*-octene, formed at 200°, has not undergone displacement of the double linking.

*General Method.*—The aliphatic sulphones were heated with sodium ethoxide as above, but only until the initial reaction ceased; in no case was the bath temperature raised above 235°. The volatile products were passed directly into bromine, the excess of which was afterwards destroyed with water and sulphur dioxide; the bromides were drawn off, dried and weighed, distilled, and in some cases analysed. The sulphinic acids were isolated in the form of their silver salts, as described in Part III. The treatment of phenyl- $\beta$ -phenylethylsulphone was different. In order to avoid the risk of the nuclear bromination of styrene by an excess of bromine, the hydrocarbon was collected as such in a trap containing water at 0°, and then extracted with chloroform; the dried chloroform solution was treated with dry bromine in chloroform until coloured, and the styrene dibromide, obtained on evaporation, was identified and

weighed. The benzenesulphinic acid was isolated, as such, from the residue by acidification of its aqueous solution and extraction with ether.

*Results.*—These are recorded in tabular form. The *silver* salts, the analytical data for which are italicised, are new.  $\alpha\beta$ -Dibromo-n-octane also is new, since, although it was prepared and analysed by Ingold and Vass in connexion with their work on quaternary ammonium hydroxides, the description and data were inadvertently omitted from the paper.

Sulphone. §	Olefin dibromide.						Silver sulphinate.					
	Yield		Found.		Calc.		Yield		Found.		Calc.	
			C	H	C	H			C	H	C	H
	%.	B. p.	%.	%.	%.	%.	%.	%.	%.	%.	%.	%.
1	91	—*	—	—	—	—	72†	—	—	—	—	—
2	77	130—132°	12.9	2.2	12.8	2.1	62	—	—	—	—	—
7	76	139—141	18.2	3.1	17.8	3.0	60	16.4	3.4	16.7	3.3	3.3
8	77	160—164	22.0	3.5	22.2	3.7	62	20.9	3.9	20.9	3.9	3.9
11	61	148—152	21.8	3.5	22.2	3.7	54	20.7	4.0	20.9	3.9	3.9
10	73	178—182	—	—	—	—	65	24.5	4.7	24.7	4.5	4.5
9	70	240—242†	35.3	5.8	35.3	5.9	62	33.4	6.2	33.7	6.0	6.0

\* M. p. and mixed m. p., 73—74°.

† Yield of free benzenesulphinic acid, m. p. and mixed m. p., 82—84°.

‡ Very pale yellow oil when freshly distilled; darkens on keeping.

§ The numbers denote the sulphones named in the first table.

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[Received, February 19th, 1930.]

#### XCIV.—Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part VIII. The Methylenic and Paraffinic Degradations of Sulphones.

By CHRISTOPHER KELK INGOLD and JOE ARTHUR JESSOP.

THE following scheme summarises the three known ways in which a radical may be eliminated as a hydrocarbon in the thermal degradation of an "onium" hydroxide. The table also indicates the conclusions which have been reached with regard to the characteristics of the ejected radical which favour each mode of elimination and the changes necessitated in the electron-groups (Hanhart and Ingold, J., 1927, 997; Ingold and Vass, J., 1928, 3125; Fenton and Ingold, J., 1929, 2342; Ingold and Jessop, *ibid.*, p. 2357).

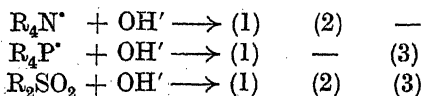


## Eliminated radical.

Elimination reaction.	Eliminated as	Structural requirement.	Facilitation by electron-sink at	Valency octets of	
				"onium" element.	hydrocarbon radical.
(1) Olefinic	R minus $H_\beta$	$H_\beta$	$C_\beta$	Preserved	Preserved
(2) Methylenic	R minus $H_\alpha^*$	$H_\alpha$	$C_\alpha$	Preserved	To sextet
(3) Paraffinic	R plus $H_\alpha$	—	$C_\alpha$	To decet	Preserved

\* The bivalent carbon compound may polymerise or isomerise.

Reaction (1), which preserves all octets, is common to ammonium and phosphonium hydroxides. In the former series, when the constitutional conditions inhibit (1) and strongly favour (2) and (3), the observed reaction is (2), and not (3); this is connected with the presumed inability of nitrogen to enlarge its octet (Sidgwick). In the latter series, when (1) is suppressed, the observed reaction is not (2), but (3); it is inferred that the phosphorus octet has a considerable tendency towards enlargement. Fenton and Ingold have shown (J., 1928, 3127; 1929, 2338; preceding paper) that sulphones in the presence of alkali undergo reaction (1); it remained to discover which type of decomposition, (2) or (3), would supervene when (1) was inhibited. The answer, contained in this paper, is that both occur; and that sulphone sulphur apparently shares, on the one hand, the tendency of phosphonium phosphorus to enlarge its electron group, and, on the other, the ability of ammonium nitrogen to deplete the electron group of a neighbouring carbon atom:



The following table summarises the observations. In two of the sulphones examined, no  $\alpha$ -hydrogen atom was present and methylenic degradation was therefore impossible; these underwent paraffinic decomposition. In the remaining five examples an  $\alpha$ -hydrogen atom was present, and both reactions were shown to proceed side by side, with the exceptions that in one case the evidence for paraffinic degradation, and in another the evidence that the same decomposition occurs in a second direction, is incomplete (indicated by parentheses in the table). It should also be mentioned that whereas the extrusion of methylene and benzyldiene was diagnosed by the recovery of ethylene and stilbene respectively, the bis-*oo'*-diphenylene-ethylene into which fluorenylidene would be expected to pass was not isolated as such, but as diphenyl-*o*-carboxylic acid, into which the unsaturated hydrocarbon is known to pass in the presence of alkali under the conditions employed.

	Sulphone $RR'SO_2$ .		Group eliminated as hydro-carbon.	
	Group R.	Group R'.	Reaction (2).	Reaction (3).
$H_a$ absent	{ Phenyl <i>p</i> -Tolyl	Phenyl 9-Phenyl-9-fluorenyl		Phenyl Phenylfluorenyl
	{ <i>p</i> -Tolyl Benzyl	9-Fluorenyl Benzyl	Fluorenyl Benzyl	Fluorenyl (Benzyl)
$H_a$ present	{ Phenyl Methyl	Benzyl Benzyl	Benzyl Benzyl	Benzyl Benzyl
	{ Methyl	<i>p</i> -Tolyl	Methyl	Methyl ( <i>p</i> -tolyl)

In the above series methylenic elimination (reaction 2) has been observed with three groups, namely, fluorenyl, benzyl and methyl. In the ammonium hydroxide series, apparently only the first of these is capable of this form of extrusion: stilbene and ethylene have never been proved to arise in the decompositions of ammonium hydroxides containing only benzyl or methyl groups. Furthermore, the direction of the methylenic decomposition of benzylmethylsulphone shows that the reaction is more prone to occur with the benzyl than with the methyl group. Hence the complete order of facility of methylenic extrusion is 9-fluorenyl > benzyl > methyl; which is the order of anionic stability, as the theory of the reaction demands (Fenton and Ingold, J., 1929, 2342; Ingold and Jessop, *loc. cit.*). This statement will be understood to relate only to *one* of the several factors which it would be necessary to envisage in a *general* discussion of bivalent carbon stability.

As regards the paraffinic degradation of sulphones (reaction 3), it need be stated only that the order in which the radicals examined tend to this form of elimination is consistent with that found in connexion with the thermal decomposition of phosphonium hydroxides. Actually the relation, fluorenyl > simple aryl, is additional; but it constitutes a further confirmation of the view that tendency to ejection increases with the anionic stability of the group.

#### EXPERIMENTAL.

*Preparation of Sulphones.*—9-Bromofluorene (10 g.) was heated for 15 minutes on the steam-bath with a solution prepared from sodium *p*-toluenesulphinate dihydrate (12 g.) and alcohol (20 c.c.). Sodium bromide separated, and the mixture was evaporated to dryness, and the residue heated for 1 hour at 100° in a stream of dry air to dehydrate the excess of sodium salt. The dried product was extracted repeatedly with boiling benzene until the extracts failed to crystallise on cooling. 9-Fluorenyl-*p*-tolylsulphone separated in iridescent plates (12.5 g.), m. p. 226–227° (Found: C, 75.2; H, 5.2.  $C_{26}H_{16}O_2S$  requires C, 75.0; H, 5.0%).

9-Hydroxy-9-phenylfluorene was prepared as described by Ullmann and Würstemberger (*Ber.*, 1904, 37, 73), and purified by crystallising it twice from carbon tetrachloride (compare Kliegl,

*Ber.*, 1905, **38**, 288), crushing the solvated crystals, and air-drying the powder over-night at 40°. The product had m. p. 85–87° and, notwithstanding the observed efflorescence, appeared still to contain solvent of crystallisation. A warm solution of the product (18 g.) in glacial acetic acid (18 c.c.) was treated with a warm solution (18 c.c.) of hydrogen bromide in the same solvent (600 g./l.), and the non-homogeneous mixture was rapidly stirred until solid appeared and then heated at 80° for 0.5 hour. The product (20 g.) obtained by filtering the cooled solution and washing the precipitate with cold glacial acetic acid had m. p. 99–100°, and, after crystallisation from ligroin, m. p. 101–101.5° (compare Staudinger, *Ber.*, 1906, **39**, 3060). A further quantity (1 g.) was recovered by adding a limited amount of water to the acetic acid solution.

When this bromide was treated with an alcoholic solution of hydrated sodium *p*-toluenesulphinate, as in the preceding preparation, the product was 9-ethoxy-9-phenylfluorene. Sodium *p*-toluenesulphinate (8 g.), dried at 100°, was therefore boiled for 40 hours with a solution of the bromide (12 g.) in dry benzene (50 c.c.). The suspension was filtered while hot, and the residue extracted with hot benzene until it became completely soluble in water.

The 9-phenyl-9-fluorenyl-*p*-tolylsulphone, which was crystallised twice (8.0 g.), separated from benzene in needles or stout prisms, m. p. 211–212° (Found: C, 78.7; H, 5.3.  $C_{26}H_{20}O_2S$  requires C, 78.8; H, 5.1%).

*Decomposition with Potassium Hydroxide.*—The reactions were carried out by the general method illustrated in the earlier papers by Fenton and Ingold.

The degradation of diphenylsulphone has already been described by Otto (*Ber.*, 1886, **19**, 2425), who observed the formation of phenol as a main product but did not record the production of benzene. Under corresponding conditions we find that both benzene (identified as the *m*-dinitro-derivative) and phenol (benzoyl derivative) are formed in quantity, and that, at temperatures below that at which benzenesulphinic acid would be largely decomposed, this acid is absent but benzene is formed and benzenesulphonic acid and phenol are also present. The initial fission products are therefore benzene and benzenesulphonic acid, not phenol and benzenesulphinic acid.

The volatile products from the decomposition of 9-phenyl-9-fluorenyl-*p*-tolylsulphone (6 g.) consisted of toluene (0.3 g.; 2:4-dinitro-derivative) and 9-phenylfluorene (0.1 g.; sublimed under reduced pressure as needles, m. p. and mixed m. p. 146–147°). The aqueous extract of the non-volatile portion yielded a small amount of cresol (qualitative tests), which was extracted with

ether after the solution had been treated with carbon dioxide, and *p*-toluenesulphinic acid (1.5 g., m. p. and mixed m. p. 88–89°), which was similarly extracted after acidification. The non-volatile product which was insoluble in water consisted of a brown resin: this was converted into a pale yellow powder by boiling with dilute aqueous ammonia and extracted several times with boiling alcohol, which removed most of the colouring matter. The dried substance (free from nitrogen and sulphur) separated in a solid form resembling lycopodium when its solution in hot chloroform-acetic acid was cooled, but the material, which decomposed above 300° and did not reduce cold permanganate in moist benzene-acetone, did not appear to be crystalline: the microscope revealed small clusters of nearly spherical particles. Considering the difficulties of purification, the analysis [Found: C, 94.0; H, 5.4; *M*, by Rast's method, 932. (C<sub>19</sub>H<sub>12</sub>)<sub>4</sub> requires C, 95.0; H, 5.0%; *M*, 960] appears to show that the substance is a hydrocarbon. Its formation seems analogous to that of the product (C<sub>19</sub>H<sub>14</sub>)<sub>2</sub> obtained by Nef by the action of triethylamine on triphenylmethyl bromide (*Annalen*, 1899, 309, 168). The 9-phenylfluorene required for comparison was prepared from 9-bromo-9-phenylfluorene (2 g.) and thin amalgamated aluminium foil (2 g.) in moist ether (50 c.c.). After being kept for 2 hours at the ordinary temperature, the solution was filtered, dried, and evaporated, and the residue crystallised from alcohol, from which the hydrocarbon separated in feathery needles, m. p. 146–149°. Its solution in ether is strongly fluorescent.

The volatile decomposition products from 9-fluorenyl-*p*-tolylsulphone on fractionation yielded toluene (25%, identified as 2:4-dinitro-derivative) and fluorene (43%), and a further 2% of fluorene was obtained by sublimation at 100° from the brown resin (6% of the weight of the sulphone) constituting the benzene-soluble portion of the non-volatile residue. The aqueous extract of the residue yielded cresol (10%, identified as benzoate), which was extracted with ether after the solution had been treated with carbon dioxide. Acidification of the residual aqueous solution yielded a white precipitate, m. p. 110–112°, consisting of diphenyl-2-carboxylic acid (yield, 15%): it crystallised from ether-ligroin in stout prisms and its solution in concentrated sulphuric acid yielded pure fluorenone (m. p. and mixed m. p.) on dilution with water. This establishes the identity of the acid, which was confirmed by comparison with a specimen obtained from fluorenone, and also with one prepared by the action of hot concentrated potassium hydroxide solution on bis-*oo'*-diphenyl-ethylene. Extraction of the acid filtrate with ether yielded *p*-toluenesulphinic acid (20%), m. p. 89–89.5° (the

recorded m. p. of this acid is 85°, but our numerous specimens all had m. p. 89°).

Phenylbenzylsulphone yielded liquid and solid hydrocarbons, of which the latter was identified as stilbene (m. p. and mixed m. p.; yield, 48%). The liquid hydrocarbons, b. p. 80–105°, were heated in a closed tube with 3% permanganate solution for 4 hours; benzene was then recovered by distillation and converted into its dinitro-derivative, and the presence of toluene in the original mixture was diagnosed by the isolation of benzoic acid by ether-extraction of the decolorised, filtered, and acidified aqueous solution. The alkaline residue from the decomposition yielded sulphur dioxide and phenol.

Dibenzylsulphone yielded toluene, stilbene, and sulphur dioxide.

Benzylmethylsulphone yielded the same products together with methanesulphinic acid and a very small amount of gas. The methanesulphinic acid was isolated as its *silver* salt by the method previously described for propanesulphinic acid (J., 1929, 2340) except that aqueous alcohol was used for the precipitation and crystallisation (Found: C, 6.6; H, 1.75.  $\text{CH}_3\text{O}_2\text{SAg}$  requires C, 6.4; H, 1.6%).

*p*-Tolylmethylsulphone yielded toluene (yield, *ca.* 25%; identified as 2:4-dinitro-derivative), *p*-cresol (*ca.* 30%; identified as benzoate), *p*-toluenesulphinic acid (18%; m. p. and mixed m. p.), and a gas which was swept over with nitrogen and shown to contain methane (13%), ethylene (27%), and a substantial quantity of hydrogen.

We wish to thank the Royal Society for a grant in aid of this investigation.

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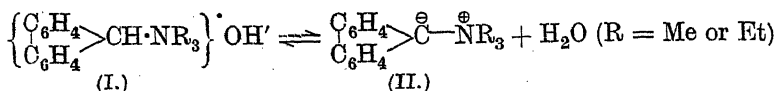
[Received, February 19th, 1930.]

*XCV.—Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part IX. Isolation of a Substance believed to contain a Semipolar Double Linking with Participating Carbon.*

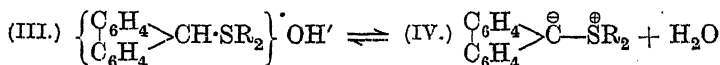
By CHRISTOPHER KELK INGOLD and JOE ARTHUR JESSOP.

IN Part VI it was noted (J., 1929, 2357) that, whilst fluorenyl-9-trimethylammonium and fluorenyl-9-triethylammonium bromides are colourless, the aqueous solutions of the corresponding hydroxides are coloured; and the suggestion was made (p. 2359, footnote) that

in either case the hydroxide (I) might be in equilibrium with an anhydride (II) which, since it contains unshared carbon electrons, would probably be coloured and highly reactive. The special structural feature of (II) is the semipolar double linking with carbon at its negative end, and since no compound containing a semipolar double bond between carbon and another element has hitherto been described, attempts were made to isolate the coloured substance:



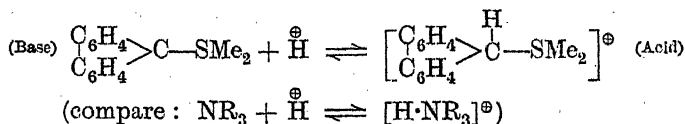
At the outset it was obvious that (II) could not be present in high concentration, for if it were it should be precipitated; it was not precipitated and the coloured solution was strongly alkaline. Probably the low concentration and the instability of the compound (see Part VI) conspired to defeat the attempts at isolation. We reflected, however, that (II) is analogous to the trialkylamine oxides,  $\overset{\ominus}{\text{O}} - \overset{\oplus}{\text{N}}\text{R}_3$ , which have low thermal stability and a strong tendency to combine with water to form trialkylhydroxylammonium hydroxides,  $\{\text{OH} \cdot \text{NR}_3\}^{\cdot} \text{OH}'$ , analogous to (I); and, further, that dialkylsulphoxides,  $\overset{\ominus}{\text{O}} - \overset{\oplus}{\text{S}}\text{R}_2$ , have much higher thermal stability and exhibit very little tendency to effect an analogous union with water. It followed that a study of the corresponding fluorenyl-sulphonium compounds (III and IV) might reveal an equilibrium much more favourable to the form which it was desired to isolate, and that the anhydride (IV), despite its negative carbon, might possess sufficient thermal stability to permit of isolation:



The initial difficulty here was to prepare a fluorenyl-9-dialkylsulphonium salt. 9-Bromofluorene and dimethyl sulphide showed little tendency to combine either in ether or in benzene or without a solvent; furthermore, attempts to prepare 9-fluorenyl mercaptan by the action of alkali sulphides on 9-bromofluorene led to the formation of 9:9-difluorenyl. At this juncture Richardson and Soper's paper appeared (J., 1929, 1873) in which their cohesion principle was enunciated; perusal of this memoir made it immediately obvious (a) that the combination of 9-bromofluorene with dimethyl sulphide should be strongly catalytically accelerated by a solvent of high cohesion, and (b) that the tendency to thermal decomposition of the required sulphonium bromide, which sets a limit to the temperatures that can be used in its synthesis, would be reduced by such a solvent. Actually, effect (a) was so powerful

that there was no need to make use of the presumed increased stability of the product at high temperatures : we mixed the reagents in nitromethane at the ordinary temperature and observed a rapid and almost quantitative formation of the sulphonium bromide. Several other successful applications of the cohesion principle have since been made in these laboratories, and there can be no doubt about its practical utility in the replacement of empirical by rational technique in synthetic operations.

When a solution of *fluorenyl-9-dimethylsulphonium bromide* was treated with excess of silver oxide, the filtrate was practically neutral. When sodium hydroxide or aqueous ammonia was used instead of silver oxide, *dimethylsulphonium 9-fluorenylidide* (IV; R = Me) was obtained as a yellow crystalline precipitate. It was sufficiently stable to admit of analysis and the determination of its molecular weight in benzene, but after some hours decomposition set in with evolution of dimethyl sulphide. Details relating to the thermal decomposition of the substance are given in the experimental portion, and it will suffice to note here that, although the compound resembles sulfoxides in refusing to form a sulphonium hydroxide by addition of water, it is definitely more basic than are sulfoxides, since it at once reacts with dilute hydrochloric acid, forming the corresponding fluorenyl-9-dimethylsulphonium salt. This is essentially a reversal of the reaction whereby dimethylsulphonium 9-fluorenylidide is formed, and thus it may be said that the constitutional environment of the 9-carbon atom confers on it properties analogous to those of a nitrogen atom :



The probable mechanism underlying this conferment of nitrogen-like properties on carbon is sufficiently indicated in Part VI.

#### EXPERIMENTAL.

*Fluorenyl-9-dimethylsulphonium Salts.*—The *bromide*, irregular hexagonal plates, m. p. 133° (Found : Br, 26.4. C<sub>15</sub>H<sub>15</sub>BrS requires Br, 26.1%), was prepared, as described in the introduction, in cold nitromethane solution, from which it crystallised. The *picrate*, precipitated by addition of aqueous sodium picrate to a solution of the bromide in water, separated from hot water in needles, m. p. 149–150° (Found : C, 55.6; H, 4.0. C<sub>21</sub>H<sub>17</sub>O<sub>7</sub>N<sub>3</sub>S requires C, 55.4; H, 3.7%).

*9:9-Difluorenyl.*—Prior to the above experiments attempts were

made to prepare the same salts by way of fluorenyl mercaptan or sulphide. 9-Bromofluorene and alcoholic sodium hydrogen sulphide were kept together over-night in the cold and the solution was then distilled to half its bulk, poured into water, and made alkaline. 9-Bromofluorene and alcoholic disodium sulphide were similarly kept in the cold and then heated for 2 hours in the steam-bath and poured into water. In each case a crystalline precipitate was obtained which was recrystallised from benzene and identified as 9:9-difluorenyl by its m. p. (242—244°) and by analysis (Found: C, 94.8; H, 5.6. Calc.: C, 94.5; H, 5.5%).

*Action of Bases on Fluorenyl-9-dimethylsulphonium Bromide: Dimethylsulphonium 9-Fluorenylidide.*—(a) *Water.* The sulphonium bromide was heated on a water-bath with water for 2 hours. Dimethyl sulphide was evolved (odour) and 9-fluorenyl alcohol precipitated (m. p. and mixed m. p.). In order to substantiate the obvious explanation of this decomposition, 9-bromofluorene was similarly heated with water; 9-fluorenyl alcohol was then formed in quantity.

(b) *Silver oxide.* On addition of excess of freshly precipitated carbonate-free silver oxide to a cold aqueous solution of the sulphonium bromide, the solution remained practically neutral. Heating the suspension on a water-bath caused the evolution of dimethyl sulphide (odour) and the formation of 9-fluorenyl alcohol (m. p. and mixed m. p.), a large quantity of which separated when the filtrate from the hot suspension was cooled. Extraction of the dried silver oxide residue with benzene yielded a red gum similar in appearance and properties to the non-volatile thermal-decomposition product of dimethylsulphonium 9-fluorenylidide (below).

(c) *Soluble alkalis.* Sodium acetate and sodium carbonate gave no precipitate with an aqueous solution of the sulphonium bromide; but aqueous ammonia, barium hydroxide, and sodium hydroxide yielded *dimethylsulphonium 9-fluorenylidide* as yellow leaflets, m. p. ca. 70—75° (decomp.), on rapid heating, which were washed with water, alcohol, and ether and dried for several hours in a vacuum. It was insoluble in water and ether, slightly soluble in alcohol, and readily soluble in ethyl acetate and benzene (Found: C, 80.3; H, 6.2; *M*, cryoscopic in benzene, 215, 226.  $C_{15}H_{14}S$  requires C, 79.6; H, 6.2%; *M*, 226). The compound began to darken and develop the odour of dimethyl sulphide after exposure to the atmosphere for a few hours (sooner if placed in a closed tube), but could be kept in a vacuum for about 24 hours with little if any signs of decomposition. In solution, however, decomposition was more rapid and the above molecular-weight determination requires explanation. Preliminary experiments showed that in benzene at



its freezing point the decomposition began to be perceptible soon after solution, and that for several hours thereafter there was a steady diminution in the apparent molecular weight. The determinations were therefore plotted against time and extrapolated to zero time. A sample, dried in a vacuum for 2 hours, gave values ranging from 196 to 153 and the extrapolated value at the moment of solution was 215. Another preparation, which had been similarly dried for 16 hours, gave values falling from 209 to 183 and the extrapolated result was 226.

*Reactions of Dimethylsulphonium 9-Fluorenylidide.*—The freshly prepared compound is immediately soluble in cold dilute hydrochloric acid. The solution contains fluorenyl-9-dimethylsulphonium chloride, as is proved by the observations that it yields dimethylsulphonium 9-fluorenylidide on treatment with ammonia, and fluorenyl-9-dimethylsulphonium picrate with aqueous sodium picrate.

The nature of the non-volatile product formed in the spontaneous decomposition which takes place at atmospheric pressure and temperature could not be elucidated. The evolution of dimethyl sulphide, which became perceptible after a few hours, was apparently complete after 4 days, and the residue was a brown amorphous substance which still contained sulphur but could not be crystallised. It was wholly insoluble in hot concentrated hydrochloric acid. By use of benzene and glacial acetic acid and other solvents, various orange and red amorphous products were obtained from it, but none could be crystallised.

Similar results were obtained more quickly by heating, and in this case the dimethyl sulphide was identified by passing the evolved gases through mercuric chloride solution and identifying the precipitated additive compound,  $3\text{HgCl}_2, 2\text{Me}_2\text{S}$ , by mixed m. p. and direct comparison. When the same decomposition was carried out in a diffusion-pump vacuum connected to the top of a mercury barometer, dimethyl sulphide condensed on the mercury, the depression of which, allowing for the vapour pressure of the sulphide, showed that no gas of the type of methane or ethylene was evolved; the sulphide was afterwards collected and converted into trimethylsulphonium iodide for confirmatory identification. The resinous residue (Found: C, 88.7; H, 5.4%) contained sulphur and could not be crystallised; on being strongly heated, it gave a crystalline distillate which proved to be fluorene (m. p. and mixed m. p.).

The solubility of dimethylsulphonium 9-fluorenylidide in acids suggested that it should add on methyl iodide. The reaction was tried under various conditions, but the addition, if any, was masked by the separation of dimethyl sulphide and its conversion into

trimethylsulphonium iodide, decomp. 207—210° (Found: I, 62.5. Calc., 62.2%); the remaining product was amorphous.

The investigation has been aided by a grant from the Royal Society, whom we wish to thank.

THE UNIVERSITY, LEEDS.

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### XCVI.—*The Occurrence of Iron Pentacarbonyl in Coal Gas stored under Pressure for 30 Years.*

By JOHN ALBERT NEWTON FRIEND and REECE HENRY VALLANCE.

IN the course of a lecture at King Edward's High School, Birmingham, in 1899, at which one of the authors was present, Dr. T. J. Baker used a cylinder of compressed coal gas. Upon ignition, the flame was normal for coal gas of that period and could not be differentiated from that supplied from the mains. The cylinder was then placed aside and apparently overlooked until the spring of 1929, and the gas was then found to give a luminous and very smoky flame. As this clearly indicated that some material change had taken place in the gas during its prolonged storage, Dr. Baker very kindly handed the cylinder to us for further examination. The gas proved to be heavily charged with the vapour of iron pentacarbonyl, as proved by the following experiments, in which the term "dried" gas refers to the gas after filtration through a plug of cotton wool and passage through a drying tube containing calcium chloride.

*Experiment 1.* The dried gas was ignited at the orifice of a small glass jet, whereby a luminous, smoky flame was obtained. When a cold glass plate was held well into the luminous portion, a black deposit resulted, which consisted partly of carbon; but after treatment with dilute hydrochloric acid, the presence of iron was detected in the solution on addition of the usual reagents. If, however, the cold plate was held a short distance above the flame, a yellow to reddish-brown deposit of ferric oxide was obtained.

The cotton wool was almost imperceptibly darkened on the surface facing the exit from the cylinder, and the solution resulting from its treatment with acid responded to the tests for ferric iron, but not for ferrous. The deposit was therefore probably ferric oxide from the cylinder.

*Experiment 2.* The previous experiment was varied by interposing a wash bottle of concentrated sulphuric acid between the

drying tube and the jet. The flame was now less luminous and entirely free from smoke. It yielded no ferric oxide or other deposit, save water, to a cold plate held above the luminous zone, and only faintly blackened the plate when the latter was held lower down, probably because the acid had not completely absorbed the unsaturated hydrocarbons.

The sulphuric acid turned dark brown and, after dilution, was tested for metals. Iron alone was found, and was present in appreciable quantity.

*Experiment 3.* The dried gas was passed through a glass tube gently heated with a spirit lamp. A brilliant black mirror resulted, which almost completely dissolved in concentrated hydrochloric acid, a few black specks of carbon alone remaining. A white precipitate of ferrous chloride was obtained, which completely dissolved on dilution. Iron was the only metal present in the solution. Upon repeating the experiment with gas that had been passed through concentrated sulphuric acid, no mirror was obtained.

*Experiment 4.* The dried gas was passed through a narrow delivery tube into a wider tube suspended vertically in a glass boiling-tube and immersed in liquid air in a Dewar flask. The uncondensed gas was burned at a platinum jet. The flame was pale blue, and yielded no deposit other than water on a cold plate held either within or above the flame. Carbon dioxide was detected as a product of combustion, but, as this would result from the combustion of methane in any case, the gas was analysed to ascertain whether or not carbon monoxide was present. The analyses are given below, unsaturated hydrocarbons being determined by the bromine method, and carbon monoxide by ammoniacal cuprous chloride; the residual gas consisted of hydrogen, nitrogen, and methane.

	Dried gas from cylinder.	Uncondensed gas from Expt. 4.
CO <sub>2</sub> , % .....	0.00	0.00
Unsaturated hydrocarbons, % .....	5.75	0.00
O <sub>2</sub> , % .....	0.00	0.00
CO, % .....	7.25	8.55
Residual gas, % .....	87.00	91.45
Ratio CO : Residual gas .....	0.0833	0.0935

The higher proportion of carbon monoxide in the uncondensed gas was due to partial retention of methane in the boiling tube along with liquid ethylene (see below). The whole of the methane, however, was not condensed, since, on combustion, the residual gas yielded some carbon dioxide.

A solid deposit, pale lemon in colour, collected in the vertical tube. It melted at approximately  $-20^{\circ}$ , yielding a viscous liquid

which became amber-coloured and increased in mobility as the temperature rose to that of the room. A drop introduced into concentrated sulphuric acid decomposed with evolution of gas, and the solution, diluted with water, showed an abundance of ferrous iron but only the merest trace of ferric iron. Upon exposure to air, the liquid slowly decomposed with the formation of brown hydrated ferric oxide. These properties correspond to those of iron pentacarbonyl (Mond and Langer, J., 1891, 59, 1090; Dewar and Jones, *Proc. Roy. Soc.*, 1905, A, 76, 558). Approximately 1.25 g. of the carbonyl collected (Found: Fe, 26.5. Calc. for  $\text{FeC}_5\text{O}_5$ : Fe, 28.5%), and this was probably about half the amount contained in the cylinder at the time we received it. It was slightly contaminated with organic matter of tarry odour.

A colourless liquid had collected in the boiling tube. On removal from the Dewar flask, it boiled vigorously, its temperature as registered by a pentane thermometer being about  $-160^\circ$ . The liquid thus contained appreciable quantities of methane. The remainder was probably ethylene more or less admixed with acetylene, of which it smelled strongly. It was not further investigated.

*Discussion.*—This research is of special interest, inasmuch as it is known that the cylinder gas was, in 1899, free from carbonyl except in such traces as would not be easily detected. Hence the compound must have been produced by the prolonged influence of compressed carbon monoxide on compact iron (*i.e.*, steel) at the ordinary temperature. From the analysis of the uncondensed gas in Expt. 4, it is evident that free carbon monoxide was still present in considerable amount, and this possibly explains the absence of the lower carbonyls of iron. When freshly filled, the pressure of the gas would, in 1899, have approximated to 120 atm. As some of the gas had been used prior to storage, the pressure leading to the formation of carbonyl would probably lie between 50 and 80 atm.

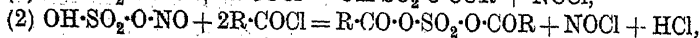
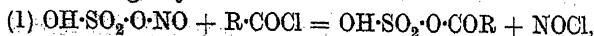
THE TECHNICAL COLLEGE,  
BIRMINGHAM.

[Received, November 20th, 1929.]

## XCVII.—*The Reaction between Acid Chlorides and Nitrosylsulphuric Acid.*

By WILLIAM JAMES DEVERALL and HARRY WILLIAM WEBB.

ACID chlorides react with nitrosylsulphuric acid in one or both of the following ways:



and the end products undergo intramolecular rearrangement, especially on heating. The results obtained with acetyl and benzoyl chlorides have already been published (Elliott, Kleist, Wilkins, and Webb, J., 1926, 1219), but confirmation of the general nature of (1) and (2) has been obtained by examination of the reactions with the three nitrobenzoyl chlorides and with phthalyl chloride. *o*- and *p*-Nitrobenzoyl chlorides react readily with nitrosylsulphuric acid, but more slowly than benzoyl chloride itself, yielding products,  $(\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O})_2\text{SO}_2$ , which are completely decomposed by water into sulphuric and nitrobenzoic acids. When these products are heated under an inert liquid, the sulphuric acid obtainable by hydrolysis decreases, the total sulphur content remaining approximately constant; at  $160^\circ$  they are completely converted into a mixture of a sulphonic acid and a sulphone, with some evolution of sulphur dioxide.

*m*-Nitrobenzoyl chloride does not react with nitrosylsulphuric acid, even at  $65^\circ$  in absence of a diluent. This may be due to the general inhibiting effect of the nitro-group on the activity of other substituents (Shoesmith, Hetherington, and Slater, J., 1924, 125, 1312), or to the setting up by this group of alternate chain polarity, but this assumption leads to the anomaly that chlorine of positive polarity is attacked while that of negative polarity is not.

All the methods of determining the relative orienting effects of various substituents in the benzene nucleus (Rule, *ibid.*, p. 1121) show that the groups containing semipolar double bonds have the least effect, and the results now obtained indicate that this is true also of the effect of such groups on the activity of other substituents in the nucleus. None of the three chloronitrobenzenes, for example, reacted with nitrosylsulphuric acid even at relatively high temperatures. On the other hand, the three chlorophenols reacted rapidly with the formation of products,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{SO}_2 \cdot \text{OH}$ , which could not be purified satisfactorily. The relative velocity of the reaction shown by measurement of the rate of evolution of nitrosyl chloride was found to be *m*- : *p*- : *o*- = 6.5 : 4 : 3.

Evidence already published (*loc. cit.*) seemed to show that the reaction of nitrosylsulphuric acid with carbonyl chlorides was preceded by the formation of an addition compound to the carbonyl group of the acid chloride. Since the oxygen in a semipolar double bond (such as  $>\text{S} \longrightarrow \text{O}$ ) occupies only one position, addition to such a bond would not be expected to take place, and hence experimental evidence bearing on the necessity for the preliminary formation of an addition product in the reaction between nitrosyl chloride and acid chlorides was obtained by an examination of certain sulphonyl chlorides and related substances. Benzene-

and toluene-sulphonyl chlorides and sulphuryl and thionyl chlorides were all found to be unattacked by the reagent. The three nitro-benzenesulphonyl chlorides were also inert unless heated to 130°, whereupon the *o*- and *p*-derivatives reacted with explosive violence, whilst the *m*-compound was inert. Since complete decomposition ensued, no conclusion can be drawn concerning possible addition. The fact that chloropicrin, which behaves in many respects as a typical acid chloride, was unattacked, also supports the hypothesis of preliminary addition, and similar evidence was obtained from the inertness of chlorides of the type RCl (R = alkyl or aryl group not containing oxygen).

Both forms of phthalyl chloride appear to yield the same end-products. This was to be expected in view of the rapidity with which the unsymmetrical high-melting form changes into the stable low-melting modification. The main reaction with both

forms appears to take the course  $C_6H_4 \begin{smallmatrix} \text{CCl}_2 \\ \text{CO} \end{smallmatrix} O + 2OH \cdot SO_2 \cdot O \cdot NO =$

$C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} O + OH \cdot SO_2 \cdot O \cdot SO_2 \cdot O \cdot NO + NOCl + HCl$  and from

the symmetrical form we isolated a small quantity of a substance  $C_6H_4(CO)_2O, H_2S_2O_7$ . The condensation products obtained in the course of this investigation have not yet been examined in detail. They were all very hygroscopic and unstable, and owing to their insolubility neither conductivities nor molecular weights could be determined.

No satisfactory explanation can be offered of the fact that groups accepted as semipolar on the basis of the octet theory are relatively inert so far as their effect on the other substituents in the molecule is concerned, but the fact that the experimental results with co-ordination compounds indicate that the linkage in the case of oxygen is more stable than a non-polar double linkage in which oxygen is involved, probably has a bearing on the matter.

#### EXPERIMENTAL.

*p*-Nitrobenzoyl Chloride and Nitrosylsulphuric Acid.—8 G. of *p*-nitrobenzoyl chloride were dissolved in 50 c.c. of dry carbon tetrachloride and warmed at 60° with 2 g. of nitrosylsulphuric acid for 4 hours. The clear liquid was decanted, and the residue washed repeatedly with carbon tetrachloride until free from the chloride, whereby a theoretical yield of *di-p-nitrobenzoylsulphuric acid* was obtained (Found : S, 7.75, 8.3, 8.0; N, 6.7.  $C_{14}H_8O_{10}N_2S$  requires S, 8.1; N, 7.1%). The analytical methods were similar to those used for the corresponding benzoyl derivative (*q.v.*), the substance being completely decomposed on boiling with dilute

hydrochloric acid into sulphuric and *p*-nitrobenzoic acids; when the evolved gases were passed through silver nitrate solution, 97.6% of the theoretical amount of chlorine was obtained.

When the substance was boiled for 3 hours in carbon tetrachloride, the amount of sulphuric acid obtainable on hydrolysis was equivalent to 5.60, 5.51% of sulphur, and the total sulphur content of the product was 7.43%. After 15 hours' refluxing, the corresponding figures were 4.10 and 7.00%. After 12 hours' heating at the boiling point of pentachloroethane (161°), no sulphuric acid was obtainable by prolonged hydrolysis of the product, which appeared to contain a sulphonic acid and a sulphone but was not examined in further detail.

*o*-Nitrobenzoyl Chloride and Nitrosylsulphuric Acid.—Considerable difficulty was found in obtaining this isomeride free from *o*-nitrobenzoic acid and repeated treatment with phosphorus pentachloride was necessary. 6.2 G. of the acid chloride were dissolved in 12 c.c. of carbon tetrachloride and warmed at 60° for 1 hour with 2.1 g. of nitrosylsulphuric acid, the resulting *di-o-nitrobenzoylsulphuric acid* being treated as above (Found: S, 8.2, 8.3%). The velocity of reaction, as measured by the rate of evolution of nitrosyl chloride, was greater than in the case of the para-compound, and some tar was formed.

*Reaction with Phthalyl Chlorides.* (With LIONEL FREDERICK BARRON.)—Nitrosyl chloride was vigorously evolved by reaction in the cold from both forms of this chloride. 30 G. of nitrosylsulphuric acid were treated with 79 g. of *s*-phthalyl chloride out of contact with air. When the reaction had ceased, the product was heated at 50–55° for 30 minutes, and then extracted repeatedly with boiling carbon tetrachloride until no further phthalic anhydride could be extracted. The residual oil solidified on cooling to a light yellow substance (Found: S, 19.3, 19.8.  $C_8H_4O_3 \cdot H_2S_2O_7$  requires S, 19.6%), which was completely decomposed on hydrolysis into sulphuric and phthalic acids. The procedure adopted in the case of *as*-phthalyl chloride was exactly similar, but no condensation product could be isolated; phthalic anhydride was recovered in high yield.

*Reaction with o- and p-Nitrobenzenesulphonyl Chlorides.* (With CHARLES KENNETH WILLIAMS.)—The chlorides were prepared by a modification of Limpricht's method (*Annalen*, 1875, 177, 60). 200 G. of benzene were added slowly to 300 c.c. of fuming sulphuric acid with cooling below 80°; after 2 hours the uncombined benzene was separated, and nitric acid (*d* 1.5) slowly added with constant shaking until no further action was apparent. The product was poured into water and filtered. The filtrate was saturated with

milk of lime, and the filtered solution evaporated and fractionally crystallised. (a) The first crop was boiled with potassium carbonate, and the evaporated filtrate yielded a potassium salt which was converted into the chloride by grinding with phosphorus pentachloride. The mass was washed well with water and extracted with ether; when the extract was dried with calcium chloride, and the ether partly evaporated, the *m*-nitrobenzenesulphonyl chloride crystallised. (b) The middle crop of crystals of the calcium salts from the mother-liquor yielded the *o*-compound by similar treatment, and the final crop yielded a mixture of the *o*- and *p*-compounds, from which the former crystallised on standing, leaving the latter as an oil.

All three isomerides were treated with nitrosylsulphuric acid under conditions precisely similar to those used for the corresponding nitrobenzoyl chlorides, but no evolution of nitrosyl chloride could be detected. When heated at higher temperatures ( $130^{\circ}$ ), the *o*- and *p*-compounds reacted with explosive violence, with rapid evolution of nitrosyl chloride; the *m*-compound was unattacked at  $130^{\circ}$ , and at temperatures sufficiently high to cause reaction it was so explosive that no product other than sulphur trioxide and *m*-nitrobenzenesulphonic acid could be isolated.

A number of aliphatic and aromatic chlorides (*e.g.*, carbon tetrachloride, pentachloroethane, chlorobenzene, and benzyl chloride) were also examined under conditions similar to those used for the nitrobenzoyl chlorides and also at the higher temperatures used for the sulphonyl chlorides. No evolution of nitrosyl chloride could be detected in any case.

*Reaction with Chlorophenols.*—5 G. of the chlorophenol were warmed to  $50^{\circ}$  with 4.5 g. of nitrosylsulphuric acid in the presence of 50 c.c. of carbon tetrachloride. A vigorous reaction with rapid evolution of nitrosyl chloride ensued. The solid was separated and washed with carbon tetrachloride as previously described. The production of tar was far greater than in any other condensation examined, and owing to the instability of the product purification was unsatisfactory.

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XCVIII.—*Studies in Polymorphism. Part I. A Preliminary Investigation of the Polymorphism of o-Nitroaniline.*

By JOHN FREDERICK JAMES DIPPY and NORMAN HOLT  
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WHILST studying the influence of various factors on the degree of supercooling of *o*-nitroaniline, one of us (J. F. J. D.) noticed that on certain occasions, notably when supercooling was large or the rate of cooling rapid, the solid was much lighter in colour than was normally the case. Suspecting polymorphism, we examined the behaviour of the substance during its crystallisation in a thin film between a microscope slide and a cover-slip, and found that it does, in fact, crystallise in two forms. Under ordinary conditions solidification starts from a number of nuclei and proceeds from them radially in the form of closely packed needles. Viewed by transmitted light, some of the resulting spherulites are seen to be composed of dark orange crystals, and the remainder of yellowish-green crystals. These two forms have been examined crystallographically under the microscope by Mr. Alan Stuart, of the Geology Department of this College, who reports as follows: "The dark orange crystals—length direction is the direction of fast vibration, pleochroic, straight extinction, biaxial, therefore orthorhombic. The yellowish-green crystals—length direction is the direction of fast vibration, slightly pleochroic, oblique extinction of about  $24^\circ$ , therefore monoclinic or triclinic."

Difficulty was at first experienced in obtaining crystals sufficiently large for this microscopic examination, especially in the case of the green form, which normally appears in extremely fine needles. This difficulty was eventually surmounted by remelting the centre portion only of a freshly crystallised melt on a slide by means of a little circular hot plate. This gave a liquid surrounded by crystals of both forms, and on cooling, each inoculated its own species from the melt. Supercooling was thus prevented and the slow growth which took place just below the melting point resulted in comparatively large crystals.

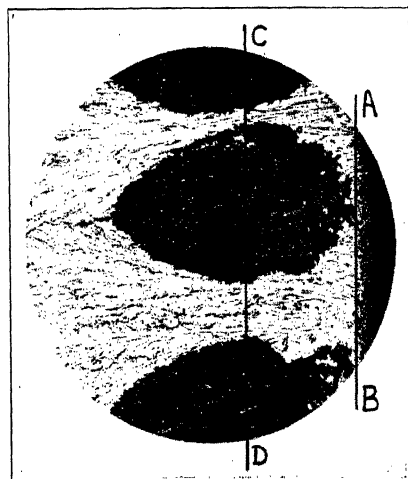
The crystal structure of *o*-nitroaniline has been studied by the X-ray method by Hermann and Burak (*Z. Krist.*, 1928, 67, 189), who concluded that it was orthorhombic. The only mention of its polymorphism appears to be a statement by Kohman, in a study of the freezing points of binary mixtures of the nitroanilines (*J. Physical Chem.*, 1925, 29, 1048), to the effect that the substance in binary mixture gave indications of existing in an unstable form.

We therefore decided to study the phenomenon in more detail, especially as the regular appearance of the two modifications side by side appeared to facilitate the investigation of certain aspects of polymorphism, such as the rate of stabilisation.

In about two hours after solidification the orange crystals are seen to have commenced to extend their territory at the expense of the green variety, showing that the former is the more stable modification. In addition, isolated crystal grains of the orange form appear in the areas occupied by the green form and continue to grow. This transformation occurs at all temperatures between that of the room and the melting point ( $70^{\circ}$ ), becoming much more rapid as the latter is approached, so within this range the polymorphism is monotropic.

The reason for the simultaneous appearance of the two forms under ordinary conditions of cooling, *i.e.*, radiation to room temperature, is that, within the temperature range in which crystallisation starts, the number of nuclei of each formed and their crystallisation velocities are of the same order, although there is usually a preponderance of the unstable form. More nearly equal quantities are produced if the slides are allowed to radiate to an atmosphere at about  $30^{\circ}$ ; and at still higher temperatures of the environment, the proportion of the stable form is increased until, just below the melting point, no unstable form at all is obtained. The main factor determining this behaviour appears to be the relationship between the crystallisation velocities of the two forms at different temperatures, which is well illustrated by Fig. 1. This photomicrograph depicts the crystallisation on a slide of some nitroaniline that had been melted except for the strip of solid to the right of the line AB, which contained both forms. On cooling, the stable (dark) form at first grew the more rapidly, as is shown by the constriction of the unstable areas; then both forms crystallised at the same speed (CD), and after this stage the stable form separated less rapidly, finally becoming entirely suppressed.

The numbers of nuclei of the two forms, however, appear to go more nearly hand in hand with alteration in the temperature, both increasing considerably as the temperature is lowered. On a slide, a melt which is rapidly cooled or greatly supercooled, appears to the naked eye to crystallise rapidly from a large number of nuclei of the unstable form. Microscopic examination, however, shows that there are numerous crystals of the stable form embedded in the mass, which evidently have not had a chance to grow owing to their small crystallisation velocity at the temperature of their formation. These small stable crystals are also seen under the microscope in the unstable areas of melts which have crystallised more slowly (see

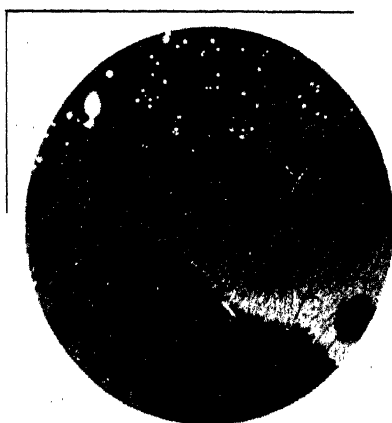


*Direction of falling temperature and crystallisation ( $\times 20$ ).*

FIG. 1.



*Soon after crystallisation.*



*21 Hours later.*

*"Crude" o-nitroaniline (the dark material is the stable form) ( $\times 5$ ).*

FIG. 2.



*Soon after crystallisation.*



*21 Hours later.*

*o-Nitroaniline twice recrystallised from alcohol ( $\times 5$ ).*

*(The stable form here appears lighter than the unstable form owing probably to the film being thicker than in Figs. 2 and 4.)*

**FIG. 3.**



*Soon after crystallisation.*



*21 Hours later.*

*o-Nitroaniline (twice recrystallised from alcohol) + 0.9% of p-nitroaniline ( $\times 5$ ).*

*(The dark material is the stable form.)*

**FIG. 4.**

next section). They apparently give rise to the previously mentioned, isolated crystal grains visible to the naked eye after stabilisation has proceeded for some time.

*The Rate of Stabilisation.*—In the thin films studied the time taken for the transformation of all the substance into the stable form depends on two factors: (1) the linear stabilisation velocity, *i.e.*, the rate at which the boundary between the stable and the unstable form moves in a direction normal to itself, and (2) the length of the boundary. In any given specimen it may be assumed that (1) remains constant at constant temperature (provided that any impurity present is evenly distributed throughout the film), if the boundary be so long and the crystals so small that the observed effect is a statistical average of the velocities at different crystal faces. Factor (2) will depend mainly on the proportion of the stable form present as small grains, for if this is large, not only will the total length of boundary be very great at the start, but it will increase rapidly as stabilisation proceeds. We have found that both these factors are greatly affected by small variations in the degree of purity of the substance (compare Tammann, "The States of Aggregation," English transl., Constable and Co., 1926, pp. 228 *et seq.*).

The starting point of all these experiments was Schuchardt's "pure" preparation, stated possibly to contain a trace of *p*-nitro-aniline, and hence subsequently referred to as "crude." On slides made from this material and kept at room temperature, stabilisation was very slight after 21 hours (see photomicrographs, Fig. 2) and was not complete until several days had elapsed. A quantity of the crude substance was recrystallised five times from absolute alcohol, a specimen of each stage being retained and dried in the ordinary way. After about one week's storage in a calcium chloride vacuum desiccator they had lost all odour of alcohol. On slides made from these specimens, stabilisation was much more rapid than on those made from the crude substance (Fig. 3; contrast Fig. 2), and was usually complete in 24 hours, this being due to a considerable increase in both the linear stabilisation velocity and the number of small grains. From this result it appeared either (1) that the crude material contained an impurity acting as a retarding agent, or (2) that the recrystallised substance retained traces of alcohol which acted as an accelerator. The second possibility did not appear to be very probable, for the manufacturers had informed us that their product was also recrystallised from alcohol, and it was not likely to have been more completely dried than ours. However, after our specimens had been kept for 12 months in a calcium chloride desiccator, they became distinctly slower, but this appeared

to be due to a diminution in the number of small grains rather than to any alteration in the linear stabilisation velocity.

In order to test the first possibility, mixtures of some of the recrystallised specimens with about 1% of *p*-nitroaniline were made, since this was one of the most likely impurities. According to the results of Kohman (*loc. cit.*), this proportion of the *p*-isomeride lowers the f. p. of *o*-nitroaniline by about 0.6°, which is the average difference found between the purest recrystallised specimens and the crude material (see Table I, p. 731). These mixtures were intermediate between the crude and recrystallised specimens as regards both the linear stabilisation velocity and the number of small grains formed (compare Figs. 4, 3, and 2). The slowness of the crude substance is therefore not due to *p*-nitroaniline alone, although this substance may be partly responsible.

Two other methods of purification were tried, *viz.*, steam-distillation and distillation directly on to a microscope slide. The yield in the first case was small, and the product behaved as regards stabilisation in much the same way as the recrystallised specimens before prolonged drying, but was possibly a little slower. In the second case, one of the recrystallised specimens was placed in a short Pyrex test-tube held in a vertical position by being surrounded with sand contained in a large iron crucible. The latter was heated and the substance fractionally sublimed on to a series of microscope slides laid in succession on the top of the test tube. The first and middle fractions stabilised as rapidly as the recrystallised specimens, but the last fractions were exceedingly slow, the last of all being much slower even than the crude substance, only a very small amount of stabilisation having taken place after 4 days. Under the microscope these slow specimens were seen to be contaminated with a liquid, evidently a decomposition or oxidation product, for the residue in the test tube was charred. This liquid appeared to be much less volatile than the nitroaniline, for, whereas on long keeping, the latter always evaporates considerably at the edges of the cover slip, this liquid did not do so. The slowness of these specimens is evidently connected with this impurity.

In these and all other experiments described in this paper, the slides and cover-slips were treated with hot chromic or chromic-nitric acid mixture, it being ensured by the use of suitable holders that the liquid had free access to all surfaces. They were then washed with distilled water, next with conductivity water, and were finally dried in an air-oven and stored in a calcium chloride desiccator. In the later experiments, they were also steamed for a few minutes before being dried. To prevent decomposition of the substance, the hot plate used for melting the films was fitted with a thermometer

and the temperature was never allowed to rise above  $120^{\circ}$ , nor were the slides left on the plate longer than was absolutely necessary. In preparing the slides, they and the cover-slips were manipulated entirely with forceps. The progress of stabilisation was conveniently followed by projecting the slides at intervals on to a screen by means of an optical lantern.

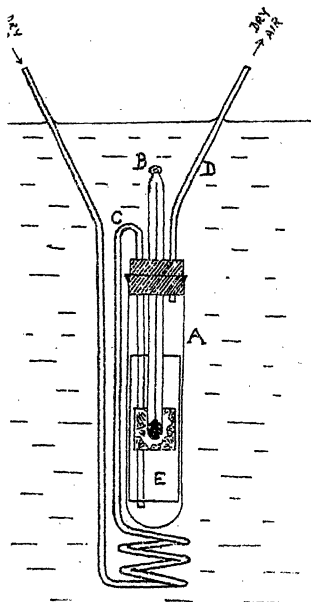
After the stabilisation process described above is complete, most slides on standing for some weeks develop dark brown patches which gradually extend. This change, which is being further studied, is partly due to the coalescence of the original needles to form larger crystals.

*Freezing Points and Melting Points.*—In order to compare the purity of the different specimens obtained by recrystallisation, an attempt was made to determine their freezing points. This proved to be impossible with the quantities available (about 2 g. of each), for the freezing point registered depended entirely on the bath temperature even when the latter was only  $1^{\circ}$  or  $2^{\circ}$  below the former. This is probably because the substance has a low velocity, or heat of crystallisation, or both. The highest temperature registered by the crude substance was  $68.7^{\circ}$  with the bath at  $67^{\circ}$ , and  $68.9^{\circ}$  with the bath at  $68^{\circ}$ . The thrice recrystallised specimen had a f. p. of  $69.2^{\circ}$  with a bath temperature of  $68^{\circ}$ , and this was the highest temperature observed. (Determinations with the fourth and fifth fractions, however, were not made.) This value may be compared with Kohman's, viz.,  $69.3^{\circ}$  (*loc. cit.*).

Attention was next directed to melting-point determinations. The m. p.'s given in the literature vary from  $68^{\circ}$  to  $71.5^{\circ}$ . The ordinary methods proved quite unsatisfactory, since it seemed impossible to judge with certainty to less than  $0.5^{\circ}$  the temperature at which melting began, even when the melting-point tube was observed with a low-power microscope. In order to remove any unstable form, the tubes were heated at  $60^{\circ}$  for some days, but this did not seem to make any difference. The difficulty was eventually overcome by means of the apparatus shown in Fig. 5, in which the melting of the substance on microscope slides could be observed. This method had the advantage that the melting points of both forms could be determined in one operation. The glass tube, A, which was just wide enough to contain a  $3'' \times 1''$  microscope slide, E, was fitted at the top with a rubber stopper carrying an Anschütz thermometer of the enclosed-scale type, B, graduated from  $60^{\circ}$  to  $85^{\circ}$  in  $0.2^{\circ}$  (made specially for this work by Messrs. Negretti and Zambra), and two  $\frac{1}{8}''$  copper tubes, C and D. The tube C, which was about one yard long, passed to the bottom of A, being coiled outside as shown. The tube D reached just below the

stopper. The slide was supported between the tube C and the thermometer, the bulb of the latter being opposite the centre of the substance under the cover-slip. The whole apparatus was immersed to the level shown in a 2-litre beaker containing water and fitted with a mechanical stirrer, a thermometer, and a movable 2-volt electric bulb enclosed in a frosted glass tube, by means of which any desired portion of the material on the slide could be brightly illuminated from behind. The beaker was heated by a shielded gas flame controlled by a fine adjustment. By attaching D to a filter pump

FIG. 5.



and C to a sulphuric acid wash bottle a rapid current of dry air at the same temperature as the outer bath could be drawn through A. Careful trials showed that, provided the temperature of the bath was not altered more rapidly than  $1^{\circ}$  in 10 minutes and a rapid current of air was drawn through A, the temperature registered by the thermometer kept the same, to within  $0.1^{\circ}$ , as that of the bath. Since the substance on the slide was only separated from the air stream by the thin cover-slip, it did not seem possible for it to lag behind the thermometer in acquiring the temperature of the air, especially as the slide and thermometer had approximately equal volumes and therefore approximately equal heat capacities. (As is well known, glass has very nearly

the same heat capacity as an equal volume of mercury.) If proof were needed, however, it was furnished by the fact that if the temperature of the apparatus were rapidly raised so that there was considerable lag on the part of the thermometer, then the substance on the slide melted at a very much lower reading than when slow heating was used. Thus, under conditions such that the thermometer registered the temperature of the bath, it also registered the temperature of the *o*-nitroaniline. These conditions, already specified, were adhered to during the melting-point determinations.

In carrying out a determination, a freshly crystallised slide containing both the stable and the unstable form was placed in A, and the apparatus rigidly fixed in the bath which had been previously



heated to 65—67°. If this preliminary heating were omitted, it was found that the long time taken to raise the apparatus to the m. p. resulted in complete stabilisation of the substance, so that the m. p. of the unstable form could not be observed. The air stream was then started, and the bath rapidly stirred. When the inner and outer parts were in thermal equilibrium the temperature was allowed to rise at the above-mentioned rate. A suitable portion of the slide, usually near the bulb of the thermometer, was illuminated and observed by means of a low-power microscope. The unstable areas melted first and left crystals of the stable form surrounded by liquid. One or two well-shaped crystals were selected for observation and watched carefully against an eye-piece scale in the microscope. The temperature at which they first showed signs of melting could thus be determined very sharply. The point at which the unstable form commenced to melt could not be determined so precisely, for this form, usually consisted of very small crystals packed closely together, and consequently there were no sharply defined crystal edges visible. Moreover, melting at the boundaries between the stable and the unstable form was often observed to take place at a lower temperature than that at which the bulk of the unstable form melted.\* The temperature recorded as the m. p. was that at which melting some distance from the boundary first became apparent.

Objection may be raised to this method on the ground that substances in thin films have lower melting points than when in bulk; for example, Meissner (*Z. anorg. Chem.*, 1920, **110**, 169) has shown that the m. p. of a film of myristic acid decreases by 0.3° as the thickness diminishes from 10  $\mu$  to 0.8  $\mu$ . Measurements of the thickness of four of our films taken at random gave the values 0.135, 0.155, 0.145, and 0.125 mm., which would appear to be well outside the range of this effect.

The results are given in Table I. With the exception of the crude specimen they refer to material dried for 12 months over calcium chloride.

TABLE I.

Specimen.	Crude.	Fractions of recrystallised specimens.					
		1.	2.	3.	4.	5a.†	5b.†
M. p. of unstable form.	ca. 67.9°	ca. 68.1°	68.1°	68.1° 68.2	68.3°	ca. 68.2°	68.2°
M. p. of stable form.	69.5 69.5	70.05 69.9	69.9	70.1 70.1	70.15 70.15	70.15 70.25	70.1

† Results with two different slides.

\* This may be a surface effect, or may be due to a concentration of traces of impurity at these places. It is also not impossible that, owing to differing molecular complexity, the two forms melt to give for a brief period different liquids, so that the m. p. of one is lowered by contact with the other.

The values for the 3rd, 4th, and 5th fractions show little difference, so that probably the maximum purity possible by the method of purification used was reached. From the average of these three specimens, the m. p. of the unstable form lies  $1.9^{\circ}$  below that of the stable form. The values must, of course, be higher than the true solid-liquid equilibrium temperature. Kohman's value of  $69.3^{\circ}$  seems, however, to be too low, for on one occasion it was noted that when a slide was cooled the crystals started to grow above  $69.5^{\circ}$ . Possibly his determination was influenced by the same factors as were our freezing-point determinations, for he too used a small quantity. It is also possible that his specimen was impure, for he states that sublimation was used as one of the methods of purification and as already stated this may lead to decomposition or oxidation.

*Summary.*

1. *o*-Nitroaniline exists in two polymorphs. One (m. p.  $68.1-68.3^{\circ}$ , monoclinic or triclinic) is unstable at all temperatures between that of the room and the m. p. and changes into a stable form (m. p.  $70.1-70.2^{\circ}$ , orthorhombic).

2. When the substance is crystallised in thin films, both forms are normally obtained, the relative amounts depending on the temperature at which crystallisation begins. This has been connected with the relation between the crystallisation velocities of the two forms at different temperatures.

3. The time taken for the disappearance of the unstable form has been studied with regard to (i) the linear stabilisation velocity at the stable-unstable boundary and (ii) the extent of the boundary; and the effect of impurities on both these factors has also been investigated.

4. An apparatus which enables the melting points of both forms to be determined in the same operation is described.

In conclusion, we wish to express our gratitude to Mr. Alan Stuart for his interest and assistance in the crystallographic part of this work.

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# XCIX.—The "Uniform Movement" of Flame in Mixtures of Ethylene, Propylene, or Butylene with Air.

By ELIZABETH HELEN MACLEOD GEORGESON and FRANCIS JOHN HARTWELL.

THE uniform movement of flame, the first stage in its propagation from the open towards the closed end of a tube, provides the most convenient means for comparing the speeds of inflammation of various gas mixtures. This communication presents measurements of the speed of uniform movement of flame in the whole range of inflammable mixtures of air with ethylene, propylene, or butylene. The experiments were carried out in a horizontal tube of 2.5 cm. diameter, and the results are therefore directly comparable with those already obtained for carbon monoxide and the lower members of the paraffin series (Payman, J., 1919, 115, 1446, 1454), for acetylene (Mason and Wheeler, *ibid.*, p. 578), and for hydrogen (Georgeson and Hartwell, J., 1927, 265). The limits of inflammability of the olefins named, in the conditions stated, were determined incidentally.

The apparatus and experimental procedure were similar to those described (J., 1927, 265). The use of a tube of transparent quartz, 2.5 cm. in diameter and 150 cm. long, and a quartz lens, enabled flame photographs to be taken over the whole inflammable range of each gas. The combustible gases, obtained commercially in cylinders, were purified by repeated liquefaction and fractional distillation. The butylene was a mixture, in approximately equal proportions, of  $\Delta^{\alpha}$ - and  $\Delta^{\beta}$ -isomerides (W. L. Wood, private communication). Mixtures with air were prepared over mercury in iron gas-holders and, except when otherwise stated, the gases were roughly dried by passage over calcium chloride, and contained less than 0.1% of water vapour. A sample of each mixture was taken for analysis from the tube prior to ignition. The mixture was fired by passing a spirit-lamp flame, 2—3 cm. high, across the opened flanged end of the tube. Photographs were taken during the progress of the flames over a distance of 12.5—38.5 cm. from the point of ignition.

The values obtained from the photographic records are given in Table I. In each case, the first column contains the percentage (by vol.) of the hydrocarbon, and the second, the speed of uniform movement (in cm./sec.).

Fig. 1 shows the results as speed-percentage curves, together with the curves for the first five paraffin hydrocarbons. For the olefins

TABLE I.

*The Speed of Uniform Movement of Flame in Mixtures.*

(Horizontal propagation in a tube 2.5 cm. in diameter.)

(i) *Ethylene-air mixtures.*

$C_2H_4$ , %	Speed.	$C_2H_4$ , %	Speed.	$C_2H_4$ , %	Speed.
3.26	No propagation				
3.30	20.6	7.05	{ 112.7, 114.7,	8.50	156.4
3.34	23.4, 22.8		{ 113.8, 156.1,	8.75	141.4, 143.9
3.36	25.8, 25.5		{ 163.3, 160.6	9.01	131.8
3.48	29.9, 28.9	7.24	{ 164.8, 165.8,	9.47	113.5
4.14	54.0, 54.8		{ 168.4, 168.7	9.51	107.3
4.33	61.0, 61.9	7.27	{ 165.0, 166.5	9.88	92.5, 91.5
4.69	74.0, 73.3	7.29	{ 162.6, 166.5	10.25	73.2, 74.4
4.97	88.5, 87.5	7.31	{ 162.3, 163.6	11.20	47.2, 47.5
5.07	92.1, 93.1	7.42	{ 165.1, 167.2	12.10	35.6, 36.3
5.42	105.6	7.58	{ 164.7, 165.7,	12.95	30.1, 31.6
5.84	119.8, 121.0		{ 163.2	14.49	23.6, 24.0
6.39	143.7, 145.1	7.61	{ 161.8, 163.4	14.66	22.7
6.40	145.8	7.66	{ 165.2, 165.8	15.50	22.7
6.81	157.6, 155.8	8.06	{ 155.1, 157.3	17.84	19.2
6.88	159.4, 158.9	8.11	{ 162.5	18.06	18.4
7.02	159.7, 153.6	8.19	{ 160.2, 157.2	18.22	18.5
		8.32	{ 151.6, 155.9,	18.30	No propagation
			{ 158.2		

(ii) *Propylene-air mixtures.*

$C_3H_6$		%.	Speed.	%.	Speed.
2.58	{ (a) No prop- agation	4.83	{ 98.0, 98.9	5.62	94.0
	{ (b) 20.85	4.95	{ 101.0, 98.2,	5.84	84.1, 90.8
			{ 99.6	6.01	82.2, 82.2
2.78	{ 28.4, 29.1,	5.04	{ 100.7, 99.6	6.31	73.3, 73.6
	{ 30.1	5.14	{ 101.9, 100.9	6.40	65.5, 68.5
3.06	38.7, 38.8	5.24	{ 100.0, 99.2	6.68	57.1, 57.8
3.42	51.9, 52.7	5.28	{ 101.5, 102.0	7.10	39.9, 40.6
3.83	70.9, 68.8		{ 99.8, 99.1	7.46	31.8, 32.3
4.14	80.1, 81.9	5.37	{ 99.3	7.56	No propagation
4.47	93.1, 91.0	5.42	{ 99.6, 99.0		

(iii) *Butylene-air mixtures.*

$C_4H_8$ , %	Speed.	$C_4H_8$ , %	Speed.	$C_4H_8$ , %	Speed.
1.93	{ (a) No prop- agation	3.65	{ 92.4, 93.5	4.65	81.0, 80.1
	{ (b) 18.9	3.78	{ 94.5, 93.5	4.94	68.1, 69.3
22.2	35.2, 33.0	3.91	{ 99.0	5.25	53.7, 53.5
2.64	53.5, 50.6	3.94	{ 96.9, 96.6	5.65	39.2, 39.2
2.83	63.6	4.08	{ 96.0, 98.2	5.96	32.5, 32.6
3.01	68.5, 68.1	4.22	{ 95.7, 94.6, 96.6	6.09	Propagation for 55 cm. only
3.35	81.4, 79.6, 83.1	4.60	{ 83.3, 82.7		

as well as for the paraffins the mixtures of maximum speed of uniform movement contain less air than is required for complete combustion. For paraffin hydrocarbons, this has been attributed to the influence of mass action (Payman, J., 1920, 117, 48), and the same explanation may be adopted for the olefins.

FIG. 1.

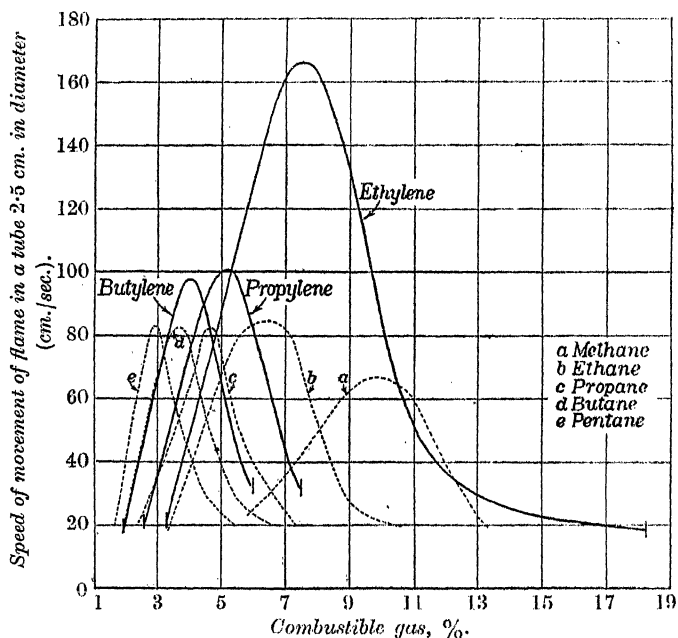


Table II shows the limits of inflammability in a horizontal glass tube, 2.5 cm. in diameter and 150 cm. long, and also the composition and speed of uniform movement of the maximum speed mixture of each hydrocarbon.

TABLE II.

	Limits of inflammability : hydrocarbon, %.		Maximum speed mixtures.		Theoretical for complete combustion : hydrocarbon, %.
	Lower limit.	Upper limit.	Hydrocarbon, %.	Speed of uniform movement (cm./sec.).	
Ethylene-air .....	3.30	18.25	7.3—7.7	166	6.51
Propylene-air ...	2.58	7.50	5.0—5.3	101	4.44
Butylene-air .....	1.93	6.0	3.9—4.1	98	3.36

A peculiarity of the ethylene-air curve is the flattening towards the upper limit.

Chapman (J., 1921, 119, 1677) has given measurements of the speed of uniform movement of flame in ethylene-air mixtures. His results are from 14 to 28% lower than ours. In the course of attempts to explain the difference we found : (i) that the speeds of flame in mixtures of ethylene and air saturated with water vapour

at laboratory temperature were only slightly lower than the speeds in mixtures roughly dried by passage over calcium chloride; (ii) that ethylene, prepared in the laboratory by Newth's method (J., 1901, 79, 915) and purified by condensation of alcohol and ether vapours in vessels cooled by solid carbon dioxide and ether, gave the same flame speeds as those recorded in Table I; (iii) that the speed of uniform movement of ethylene-air mixtures was not affected by variations in length of the explosion tube.

It seemed that the cause of the difference might be found in the methods of registering the flame speeds, for Chapman had recorded automatically the time interval between the fusion of successive screen wires, whereas we had used the photographic method. The latter is now regarded as the more trustworthy, for screen wires are obstacles in the path of the flame, and, moreover, they record only the mean speed of flame between one wire and the next. We therefore fitted a tube with screen wires and made measurements by both methods simultaneously, over the same length of tube. The speed measurements agreed with one another, but were some 3—4 cm./sec. higher than corresponding figures in Table I, a result which the photographs explained by showing a small increase in flame speed near the wires, which presumably function as small constrictions in the tube. So far as we could discover, therefore, the differences between Chapman's figures and ours are not attributable to an error in either method of measurement of flame speeds.

A clue to an explanation was provided by the flame speed of the 7.05% ethylene-air mixture, which was found to be either 114 or 160 cm./sec., approximately. The lower speed was obtained when the ground-glass cap at the firing end of the tube was removed in such a manner as to cause mechanical disturbance of the mixture. Low flame speeds were also regularly induced by firing the mixture while the tube was still "ringing" after a rather sharp blow; in these circumstances speeds of 110—120 cm./sec. were obtained with a maximum speed mixture instead of the normal speed of 166 cm./sec. Mason and Wheeler (J., 1920, 117, 1233) observed a similar effect in the upward propagation of flame in certain methane-air mixtures, and attributed the effect to resonance. We are inclined, therefore, to explain the comparative slowness of Chapman's flames as being due to the incidence of resonance during part of their progress between the screen wires. The photographic registration of flame speeds prevents such an effect from being overlooked.

The upper limit of ethylene in air was found to be 18.25%. At about 14% of ethylene, the colour of the flame changed from bluish-green (below 14%) to yellow (14—18%), and carbon was liberated.

This work has been carried out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish it.

SAFETY IN MINES RESEARCH LABORATORIES,  
SHEFFIELD.

[Received, February 11th, 1930.]

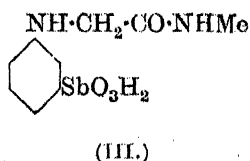
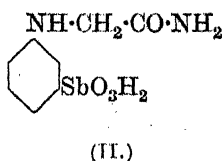
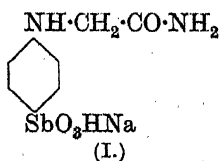
### C.—Aromatic Stibinic Acids containing Phenyl and Quinolyl Radicals.

By GILBERT T. MORGAN and JAMES WILFRED COOK.

IN recent years considerable attention has been directed towards organic antimonials as therapeutic agents in tropical medicine (Schmidt, *Ind. Med. Gaz.*, 1928, 63, 643) and the compounds now described were prepared in the course of a search for active substances of greater stability than *p*-aminophenylstibinic acid, from which many of the successful antimonials are derived.

One of the most promising arsenicals in present use is tryparsamide and Brahmachari (*Indian J. Med. Res.*, 1922, 10, 510) claimed to have isolated the analogous antimony compound (sodium *N*-phenylglycineamide-*p*-stibinate, I). We have made repeated unsuccessful attempts to prepare Brahmachari's substance, the chief difficulty being that *p*-aminophenylstibinic acid decomposes rapidly under the conditions necessary to effect condensation with chloroacetamide. Attempts to overcome this difficulty by introducing the stibinic acid group into a previously formed *N*-phenylglycine molecule (for example, by the Bart-Schmidt reaction with *p*-amino-*N*-phenylglycine or *p*-amino-*N*-acetyl-*N*-phenylglycine) also proved abortive. Moreover, *pp'*-diaminodiphenylstibinic acid and 4-hydroxy-3-aminophenylstibinic acid both decomposed when heated with chloroacetamide in faintly alkaline solution.

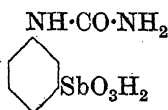
*m*-Aminophenylstibinic acid is considerably more stable than its para-isomeride and condenses smoothly with chloroacetamide and with chloroacetomethylamide to yield *N*-phenylglycineamide-*m*-stibinic acid (II) and *N*-phenylglycinemethylamide-*m*-stibinic acid (III) respectively.



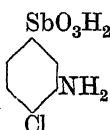
*m*-Aminophenylstibinic acid also reacted with cyanic acid to give *m*-carbamidophenylstibinic acid (IV).

4-Chloro-3-aminophenylstibinic acid (V), obtained by oxidation of 4-chloro-3-aminophenylstibinous chloride hydrochloride (Schmidt, *Annalen*, 1920, **421**, 208; *Ber.*, 1926, **59**, 556) with ammoniacal hydrogen peroxide at 0°, failed to react when its sodium salt was heated with chloroacetamide or chloroacetomethylamide in aqueous or alcoholic solution, the reactivity of the primary amino-group being probably depressed by the ortho-chlorine atom.

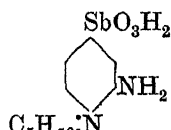
The chlorine atom in 4-chloro-3-nitrophenylstibinic acid (Schmidt, *Annalen*, 1920, **421**, 188) is considerably less reactive than that in the analogous arsenic acid (D.R.-PP. 285,604, 446,545; Barber, J., 1929, 471), since it does not condense with pyridine or aniline at 100°, with ammonia at 120°, or with diethylamine in boiling alcoholic solution. With piperidine in boiling alcohol, however, 3-nitro-4-piperidinophenylstibinic acid was readily obtained, and this was reduced by ferrous hydroxide to 3-amino-4-piperidinophenylstibinic acid (VI).



(IV.)



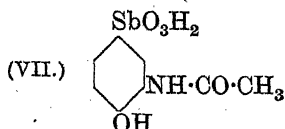
(V.)



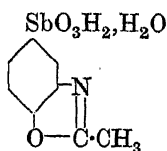
(VI.)

3-Nitro-4-ethylaminophenylstibinic acid was produced from 4-chloro-3-nitrophenylstibinic acid and ethylamine in alcoholic solution at 120—130°, the reaction being accompanied by partial elimination of antimony from the molecule.

Treatment of an aqueous suspension of 3-amino-4-hydroxyphenylstibinic acid with acetic anhydride led to the formation of a stibinic acid which was probably 3-acetamido-4-hydroxyphenylstibinic acid (VII), but its extreme solubility in water was remarkable, since most aromatic stibinic acids are very sparingly soluble, as is also the analogous arsenic acid (stovarsol), so the possibility of internal condensation to a benzoxazole derivative (VIII) is not excluded.



(VII.)

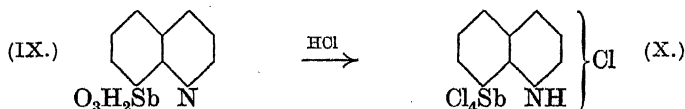


(VIII.)

The conditions necessary for the production of quinolylstibinic acids by the Bart-Schmidt reaction have been determined (compare Binz and R  th, *Eng. Pat.* 250,287) and *quinolyl-5-stibinic*, *quinolyl-6-stibinic*, and *quinolyl-8-stibinic acids* were obtained from the corresponding aminoquinolines. The stibinic acid group has less in-



fluence than the arsinic acid group in inhibiting the basic character of the quinoline residue, since these stibinic acids are soluble even in dilute acetic acid, whereas Binz and R  th (*Annalen*, 1927, 453, 240) have shown that the corresponding arsinic acids require concentrated mineral acids for salt formation. These quinolylstibinic acids were purified through their sparingly soluble crystalline *stibinic chlorides*, the salt obtained from quinolyl-8-stibinic acid (IX), for example, being represented by structure X :



By evaporation of its solution in dilute acetic acid, quinolyl-8-stibinic acid (IX) is converted into a water-soluble variety which is probably a salt formed by internal neutralisation, since the isomeric 5- and 6-compounds do not behave in this way. An attempt was made to prepare 6-methoxyquinolyl-8-stibinic acid and 6-ethoxyquinolyl-8-stibinic acid from the corresponding alkoxy-aminoquinolines, which themselves are stated to be destructive to blood parasites (*Eng. Pat.* 267,457). The yield of these stibinic acids was, however, very poor and they could not be obtained free from coloured impurities, but it is noteworthy that neither of these derivatives of quinolyl-8-stibinic acid could be converted into a water-soluble form by evaporation of dilute solutions of the acetates.

The trypanocidal action of the compounds now described has been examined by Professor Warrington Yorke under the auspices of the Chemotherapy Committee of the Medical Research Council. The substances were administered intraperitoneally and were found to possess only a slight activity against *T. equiperdum*. The minimum lethal doses (M.L.D.), expressed in mg. per 20 g. mouse, are given in the following table, sodium *m*-aminophenylstibinate being included for comparison.

Substance.	M.L.D.
Sodium <i>m</i> -aminophenylstibinate .....	25
Sodium <i>m</i> -carbamidophenylstibinate .....	25
Sodium <i>N</i> -phenylglycineamide- <i>m</i> -stibinate .....	20
Sodium <i>N</i> -phenylglycinemethylamide- <i>m</i> -stibinate .....	30
Acetylated 3-amino-4-hydroxyphenylstibinic acid (VII or VIII) ...	10
Sodium quinolyl-5-stibinate .....	1.8
Sodium quinolyl-6-stibinate .....	3.6
Quinolyl-8-stibinic acid .....	0.9

## EXPERIMENTAL.

### I. Derivatives of *m*-Aminophenylstibinic Acid.

*m*-Carbamidophenylstibinic Acid (IV).—*m*-Aminophenylstibinic acid (6 g.) was dissolved in *N*-hydrochloric acid (20 c.c.), and the

excess of mineral acid neutralised with sodium hydroxide. 2*N*-Acetic acid (25 c.c.) was added, followed by a concentrated aqueous solution of potassium cyanate (2.5 g.) at 0°. After an hour the precipitate was collected and reprecipitated by hydrochloric acid from its solution in sodium hydroxide. For purification, the product (5.5 g.) was suspended in concentrated hydrochloric acid (50 c.c.) at 0°. After 3 hours the yellow crystalline stibinic chloride was collected, washed with hydrochloric acid, and hydrolysed by water to the stibinic acid, which was washed with water to remove occluded salts and finally dried in a vacuum desiccator. *m*-Carbamidophenylstibinic acid, a white amorphous powder, decomposed on heating, without melting\* (Found: N, 9.5.  $C_7H_7O_3N_2Sb, H_2O$  requires N, 9.1%).

The sodium salt, precipitated on adding alcohol to its neutral solution, formed a white amorphous powder, moderately easily soluble in water (Found: Sb, 39.0.  $C_7H_5O_4N_2NaSb$  requires Sb, 37.0%). Most of the sodium salts gave high analytical figures for antimony. This accords with the observations of Fargher and Gray (*J. Pharm. Exp. Ther.*, 1921—1922, 18, 341), who cite several instances of neutral sodium aryl stibinates containing less than one atom of sodium per molecule.

*N*-Phenylglycineamide-*m*-stibinic Acid (II).—A solution of *m*-aminophenylstibinic acid (5.2 g.) and chloroacetamide (3.6 g.) in *N*-sodium hydroxide (20 c.c.) was heated at 90° for 1½ hours. Sufficient sodium hydroxide was added to dissolve the resulting resinous precipitate and the solution, which still gave a reaction for primary aromatic amine, was treated with a further 1.5 g. of chloroacetamide and heated for another hour to complete the condensation. The clear solution obtained by adding the requisite amount of alkali was acidified with acetic acid, the precipitated stibinic acid was dissolved in 2*N*-hydrochloric acid (15 c.c.), and addition of ice-cold hydrochloric acid (*d* 1.19; 15 c.c.) then resulted in separation of the crystalline stibinic chloride. This chloride was rapidly collected and dissolved in water, the solution made alkaline, and the free stibinic acid reprecipitated by acetic acid (Found: Sb, 39.5; N, 9.0.  $C_8H_9O_3N_2Sb, 1/3H_2O$ † requires Sb, 39.4; N, 9.1%). *N*-Phenylglycineamide-*m*-stibinic acid, a white amorphous powder, was readily soluble in dilute alkali or excess of dilute mineral acids but insoluble

\* None of the stibinic acids described in the sequel had a definite melting point.

† Schmidt (*loc. cit.*) has shown that the vacuum-dried aryl stibinic acids are usually represented by formulæ of the type  $3ArSbO_2, H_2O$  or  $3ArSbO_2, 2H_2O$ . The figures for antimony which we have obtained have led us to adopt similar formulations, although with considerable reserve on account of the instability and difficulty of purification of the compounds.

in dilute acetic acid. When added to its dilute hydrochloric acid solution, sodium nitrite precipitated a gelatinous nitrosoamine.

The *sodium* salt, precipitated by addition of alcohol to its concentrated neutral aqueous solution, was a white amorphous powder readily soluble in water (Found: Sb, 35.9.  $C_8H_{10}O_4N_2NaSb$  requires Sb, 35.5%).

*Sodium N-Phenylglycinemethylamide-m-stibinate* (III).—Condensation of *m*-aminophenylstibinic acid with chloroacetomethylamide was carried out exactly as with chloroacetamide, a double heating with the methylamide being also necessary for complete reaction. Phenylglycinemethylamide-*m*-stibinic acid, when purified through the stibinic chloride, had properties similar to those of the corresponding amide, and gave a strong odour of methylamine when heated with sodium hydroxide solution. The *sodium* salt, which was isolated from its concentrated aqueous solution by addition of alcohol and ether, formed a white amorphous powder completely soluble in about half its weight of water (Found: Sb, 33.1.  $C_9H_{12}O_4N_2NaSb$  requires Sb, 34.1%).

Condensation of *m*-aminophenylstibinic acid with chloroacetylamine proceeded smoothly with the formation of an acid, of which the sodium salt was not precipitated from its aqueous solution even by alcohol and ether.

*pp'-Diacetamidodiphenylstibinous Hydroxide*.—A suspension of *p*-acetamidophenylstibinous chloride hydrochloride (10 g.) in 0.005*N*-sodium hydroxide (1000 c.c.) was boiled for an hour. The solution, filtered hot from antimony oxide, deposited colourless needles on cooling; these, recrystallised from aqueous methyl alcohol, intumesced at 128° (Found: Sb, 29.5. Calc.: Sb, 29.9%). This process is simpler than Schmidt's method of degradation of the triacetamidotriphenylstibine (*Annalen*, 1922, 429, 137).

This secondary hydroxide was oxidised to the diarylstibinic acid by Schmidt's method, and the product (4 g.) hydrolysed at 0° in  $\frac{3}{4}$  hour by *N*-sodium hydroxide solution (25 c.c.). The resulting amino-compound gave only aniline and resinous products on treatment with chloroacetamide.

## II. Condensation of 4-Chloro-3-nitrophenylstibinic Acid with Amines.

*3-Nitro-4-piperidinophenylstibinic Chloride Hydrochloride*.—A solution of 4-chloro-3-nitrophenylstibinic acid (3.28 g.) and piperidine (5.5 c.c.) in alcohol (20 c.c.) was boiled for 3 hours, and the solution poured into water. The orange precipitate (3.5 g.) was dissolved in warm glacial acetic acid (20 c.c.), and the cooled solution treated with concentrated hydrochloric acid (20 c.c.). The crystalline

precipitate was washed with a mixture of hydrochloric acid and acetic acid (1 : 1) and dried over sulphuric acid and solid potassium hydroxide. The *stibinic chloride hydrochloride* formed a colourless microcrystalline powder, decomp. 185—187° (Found : Sb, 24.3.  $C_{11}H_{13}O_2N_2Cl_4Sb.HCl$  requires Sb, 24.1%).

*3-Nitro-4-piperidinophenylstibinic acid hydrochloride*, formed when the foregoing stibinic chloride was suspended in a large volume of water for several hours, was an orange amorphous powder (Found : Sb, 29.3.  $C_{11}H_{13}O_4N_2Sb.H_2O.HCl$  requires Sb, 29.4%).

*3-Nitro-4-piperidinophenylstibinic Acid*.—The hydrochloride of the acid was dissolved in alcohol with 2*N*-sodium hydroxide; the clear solution was acidified with acetic acid. After drying, the gelatinous precipitate was again washed with water to remove occluded salts and obtained as an orange amorphous powder, sparingly soluble in excess of dilute aqueous alkali (Found : Sb, 33.6.  $C_{11}H_{13}O_4N_2Sb.1/3H_2O$  requires Sb, 33.3%).

*3-Amino-4-piperidinophenylstibinic Acid* (VI).—Reduction of the nitro-compound with stannous chloride yielded no crystalline product, but the aminophenylstibinic acid was readily formed when ferrous hydroxide was used. A solution of 3-nitro-4-piperidinophenylstibinic acid (3 g.) in alcohol (15 c.c.) and 6*N*-sodium hydroxide (3 c.c.) was poured into water (150 c.c.), this procedure being adopted in order to obtain the substance in a finely divided state. More 6*N*-sodium hydroxide (30 c.c.) was added to the suspension, followed slowly by a solution of ferrous sulphate (15 g. in 100 c.c. of water). After 1½ hours the hydroxides of iron were removed and the filtrate was acidified with acetic acid. The gelatinous stibinic acid was purified through the stibinic chloride (obtained with ice-cold hydrochloric acid) (Found : Sb, 36.5.  $C_{11}H_{15}O_2N_2Sb.1/3H_2O$  requires Sb, 36.3%).

*3-Amino-4-piperidinophenylstibinic acid* formed a greyish powder, soluble in very dilute mineral acid or alkali, the solutions giving reactions for primary amine. The *sodium* salt was produced when a suspension of the acid (3 g.) in 50% alcohol (80 c.c.) was neutralised with sodium hydroxide, the filtered solution evaporated to dryness, the residue extracted with boiling methyl alcohol, and the extract evaporated to dryness. This salt was too sparingly soluble in water to be used for intravenous injection (Found : Sb, 33.9.  $C_{11}H_{16}O_3N_2NaSb$  requires Sb, 33.0%).

*3-Nitro-4-ethylaminophenylstibinic Chloride*.—A solution of 4-chloro-3-nitrophenylstibinic acid (3.28 g.) in alcoholic ethylamine (12 c.c. of a solution containing 22 g. of ethylamine per 100 c.c.) was heated at 120—130° for 3 hours. After cooling, an orange solid had separated consisting of the nitroethylaminophenylstibinic acid

mixed with antimony oxide. This crude product (1 g.) was ground under concentrated hydrochloric acid (20 c.c.) and the crystals were washed with concentrated hydrochloric acid and dried over sulphuric acid and solid potassium hydroxide. 3-Nitro-4-ethylaminophenylstibinic chloride formed a buff microcrystalline powder with no definite m. p. (Found: Sb, 28.6.  $C_8H_9O_2N_2Cl_4Sb$  requires Sb, 28.4%). This stibinic chloride was immediately hydrolysed by water to the orange 3-nitro-4-ethylaminophenylstibinic acid, obtained pure for analysis by acidifying a dilute solution of the ammonium salt with acetic acid (Found: Sb, 37.1.  $C_8H_9O_4N_2Sb \cdot 1/3H_2O$  requires Sb, 37.4%).

3-Nitro-4-methylaminophenylstibinic chloride was obtained in precisely the same manner as the ethylamino-compound from 4-chloro-3-nitrophenylstibinic acid (3.28 g.) and 15% alcoholic methylamine (15 c.c.) at 120–130° (Found: Sb, 28.8.  $C_7H_7O_2N_2Cl_4Sb$  requires Sb, 29.3%).

### III. Acetylation of 3-Amino-4-hydroxyphenylstibinic Acid.

The potassium salt (16 g.) of 3-nitro-4-hydroxyphenylstibinic acid (Schmidt, *Annalen*, 1920, **421**, 212) was reduced by sodium hydro-sulphite (D.R.-P. 270,488) to the amino-compound, which was suspended in water (12 c.c.) and acetylated by the gradual addition of acetic anhydride (9 c.c.). This treatment led to a clear solution and after 24 hours several volumes of acetone were added to precipitate the stibinic acid (VII or VIII). The substance formed a white amorphous powder extremely soluble in water with an acid reaction, insoluble in acetone, alcohol or glacial acetic acid, and yielding a sodium salt readily soluble in water (Found: Sb, 37.8.  $C_8H_8O_4NSb \cdot H_2O$  requires Sb, 37.8%).

### IV. Quinolylstibinic Acids.

The appropriate aminoquinoline (6 g.; 1/24 g.-mol.) in water (50 c.c.) and concentrated hydrochloric acid (20 c.c.) was diazotised at 0° with sodium nitrite (3 g.). The diazo-solution was added slowly, with simultaneous addition of 6*N*-sodium hydroxide (20 c.c.), to an ice-cold sodium antimonite solution prepared from antimony trichloride (12.6 g.), 5*N*-hydrochloric acid (20 c.c.), and glycerol (20 c.c.), the resulting solution being treated with 6*N*-sodium hydroxide until the precipitate first formed had just redissolved and then diluted to 800 c.c. After being kept at the ordinary temperature over-night, the solution was freed by filtration from the bulk of coloured by-products, and the filtrate acidified with acetic acid. The precipitate was suspended in concentrated hydrochloric acid (50 c.c.) and the product was collected after an hour and washed

with concentrated hydrochloric acid. The stibinic chloride, thus obtained free from antimony oxide, was decomposed by excess of dilute alkali, the stibinic acid being precipitated by acetic acid.

*Quinolyl-5-stibinic Acid.*—The crude stibinic acid (2 g. from 6 g. of 5-aminoquinoline) was converted into stibinic chloride by addition of concentrated hydrochloric acid to its solution in dilute hydrochloric acid, and the *stibinic acid* regenerated in the usual way. A small sample (0.5 g.) was further purified for analysis by extraction with boiling methyl alcohol (200 c.c.). The filtrate was concentrated to small bulk, and the deposit washed with methyl alcohol and dried (Found: Sb, 40.6.  $C_9H_6O_2NSb \cdot H_2O$  requires Sb, 40.6%). This acid formed a buff powder very sparingly soluble in most media, although moderately easily soluble in glacial acetic acid and readily soluble in dilute acids or alkalis. The *sodium* salt was obtained by adding a slight excess of sodium hydroxide to an aqueous suspension of the free acid (2.5 g.). The excess of alkali was neutralised with hydrochloric acid, and the filtrate evaporated to dryness in a vacuum desiccator. The residue was extracted with alcohol (30 c.c.), the solution filtered to remove sodium chloride, and then evaporated to dryness. This sodium salt was readily soluble in water (Found: Sb, 39.6.  $C_9H_7O_3NNaSb$  requires Sb, 37.8%).

*Quinolyl-5-stibinic chloride hydrochloride*, obtained when a solution of the purified stibinic acid in dilute hydrochloric acid was treated at 0° with concentrated hydrochloric acid, was a buff microcrystalline powder, m. p. 222° (Found: Sb, 28.2.  $C_9H_7NCl_5Sb$  requires Sb, 28.4%).

*Quinolyl-6-stibinic Acid.*—The crude stibinic acid (2 g. from 6 g. of 6-aminoquinoline) was purified through the stibinic chloride, and its filtered solution in methyl alcohol evaporated to dryness. The residual *acid* formed a buff powder moderately easily soluble in methyl alcohol and readily soluble in dilute acids or alkalis (Found: Sb, 40.1.  $C_9H_6O_2NSb \cdot H_2O$  requires Sb, 40.6%). The *sodium* salt, prepared and purified in the same manner as sodium quinolyl-5-stibinate, formed a straw-yellow powder readily soluble in water or alcohol (Found: Sb, 38.8.  $C_9H_7O_3NNaSb$  requires Sb, 37.8%).

*Quinolyl-6-stibinic chloride hydrochloride* was obtained, by the addition of concentrated hydrochloric acid to an ice-cold solution of the stibinic acid in dilute hydrochloric acid, as a buff microcrystalline powder, m. p. 237° (Found: Sb, 28.5.  $C_9H_7NCl_5Sb$  requires Sb, 28.4%).

*Quinolyl-8-stibinic Acid (IX).*—(a) *Water-insoluble form.* The crude acid (3.6 g. from 6 g. of 8-aminoquinoline) was purified in the same way as the 6-stibinic acid and formed a light brown powder moderately easily soluble in methyl alcohol, readily soluble in dilute

acids, but soluble only in excess of sodium hydroxide (Found: Sb, 41.3.  $C_9H_6O_2NSb, 2/3H_2O$  requires Sb, 41.4%).

(b) *Water-soluble form.* Purified quinolyl-8-stibinic acid (3 g.) was dissolved in 0.2*N*-acetic acid (50 c.c.), and the solution evaporated to dryness. The residue was redissolved in water, and the solution again evaporated to dryness in a vacuum desiccator. The resulting light brown powder was readily soluble in water, addition of a drop of sodium hydroxide resulting in precipitation of the insoluble form (Found: Sb, 40.2.  $C_9H_6O_2NSb, H_2O$  requires Sb, 40.6%).

*Quinolyl-8-stibinic chloride hydrochloride* (X) separated, when concentrated hydrochloric acid was added to an ice-cold methyl-alcoholic solution of the stibinic acid, in small brownish needles, decomp. 200—210° (Found: Sb, 28.4.  $C_9H_7NCl_5Sb$  requires Sb, 28.4%).

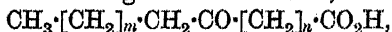
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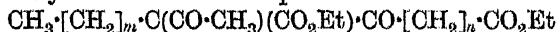
### CI.—A Synthesis of Certain Higher Aliphatic Compounds. Part III. A Variation of the Keto-acid Synthesis, constituting an Improved Method for the Extension of Normal Carbon Chains.

By (Mrs.) GERTRUDE MAUD ROBINSON.

IN Part I of this series (Robinson and Robinson, J., 1925, 127, 175), the synthesis of normal long-chain keto-acids,



by the hydrolysis of condensation products of the form



was described; the process gave only moderately satisfactory yields, owing to the fact that a varying but always a relatively considerable amount of the acid,  $CO_2H \cdot [CH_2]_n \cdot CO_2H$ , was recovered. Underlying this problem, the factors influencing the direction of fission of  $\beta$ -diketones are of fundamental importance, since it is clear that the recovery of the dibasic acid is due to hydrolysis initiated by the stage  $CH_3 \cdot [CH_2]_m \cdot C(CO \cdot CH_3)(CO_2Et) \cdot CO \cdot [CH_2]_n \cdot CO_2Et \rightarrow CH_3 \cdot [CH_2]_m \cdot CH(CO \cdot CH_3) \cdot CO_2Et + CO_2H \cdot [CH_2]_n \cdot CO_2Et$ , which competes with the desired direction of change in which the acetyl group is removed as acetic acid.

An example of such competition of acyl groups in the hydrolysis of  $\beta$ -diketones has been quantitatively studied by Bradley and Robinson (J., 1926, 2356), who found in a series of substituted dibenzoylmethanes,  $R \cdot CO \cdot CH_2 \cdot CO \cdot R'$ , that hydrolysis by alkalis

occurred with production of the stronger of the acids,  $R \cdot CO_2H$  and  $R' \cdot CO_2H$ , in preponderating amount.

This suggested two methods for the improvement of the yields in the keto-acid syntheses, namely, (a) the use of a  $\beta$ -ketonic ester,  $R \cdot CO \cdot CH_2 \cdot CO_2Et$ , such that  $R \cdot CO_2H$  is a stronger acid than acetic acid, and (b) the acylation of a substituted ethyl acetoacetate by the group related to the weakest possible acid; this could clearly be achieved by removing the terminal carboxyl group from the acyl group and introducing it at the end of the alkyl chain. Thus, an acid  $CH_3 \cdot [CH_2]_m \cdot CH_2 \cdot CO \cdot [CH_2]_n \cdot CO_2H$  can be obtained by the hydrolysis of the complexes

$CH_3 \cdot [CH_2]_m \cdot C(CO \cdot CH_3)(CO_2Et) \cdot CO \cdot [CH_2]_n \cdot CO_2Et$   
or  $CO_2Et \cdot [CH_2]_{n-1} \cdot C(CO \cdot CH_3)(CO_2Et) \cdot CO \cdot [CH_2]_{m+1} \cdot CH_3$ , and it was anticipated that the latter method would give the better yield because the dibasic acids are stronger than the fatty acids. In view of the accessibility of ethyl acetoacetate, practical effect has been given to the proposal (b) only, and actually the new process constitutes a great improvement and is applicable to the transformation of an acid  $R \cdot CO_2H$  into  $R \cdot CO \cdot CH_2 \cdot [CH_2]_n \cdot CO_2H$ , the accessory starting points being ethyl acetoacetate and  $Br \cdot [CH_2]_n \cdot CO_2Et$ . It is known (Le Sueur and Withers, J., 1915, 107, 738) that Clemmensen's method (*Ber.*, 1913, 46, 1837) can be advantageously used for the reduction of long-chain keto-acids, so we may proceed from  $R \cdot CO_2H$  to  $R \cdot [CH_2]_{n+2} \cdot CO_2H$  in a few simple stages, and can then repeat the process. The number of carbon atoms added in each stage of extension is limited only by the relative inaccessibility of the required  $\omega$ -bromo-acids, but ethyl  $\omega$ -bromodecoate can be obtained from sebacic acid and ethyl  $\omega$ -bromoundecoate from undecenic acid (Walker and Lumsden, J., 1901, 79, 1191), so an extension of 11 or 12 carbon atoms in each cycle of operations is quite feasible.

It is hoped that this development will be described in subsequent communications, and in the present memoir the conversion of certain acids,  $R \cdot CO_2H$ , into  $\gamma$ -keto-acids,  $R \cdot CO \cdot CH_2 \cdot CH_2 \cdot CO_2H$ , and the related alkylbutyrolactones is recorded.

Undecoic, undecenic and elaidic acids were converted into the chlorides and condensed with the sodium derivative of ethyl aceto-succinate in ethereal solution; the products were hydrolysed by means of dilute aqueous potassium hydroxide, at first in the cold and later on the steam-bath, and good yields of the keto-acids resulted.

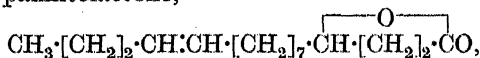
By using benzoyl chloride,  $\beta$ -benzoylpropionic acid was obtained in about 41% yield, but  $\beta$ -o-nitrobenzoylpropionic acid could not be prepared by this method. This is in accord with anticipation



based on the theory already mentioned, and, from the same point of view, the failure to prepare a keto-dibasic acid by hydrolysing the ester  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{CO}\cdot\text{CH}_3)(\text{CO}_2\text{Et})\cdot\text{CO}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{Et}$  is explicable. There is no further reference to these negative results in the experimental section.

The preparation of a diketo-acid succeeded, but, again, the keto-acids are stronger than the fatty acids and, as expected, the yield was poor. For this example, 10-*ketotridecoic acid* was synthesised by an application of the method of Parts I and II; its chloride and ethyl sodioacetosuccinate afforded an ester,

$\text{CH}_3\cdot[\text{CH}_2]_2\cdot\text{CO}\cdot[\text{CH}_2]_8\cdot\text{CO}\cdot\text{C}(\text{CO}\cdot\text{CH}_3)(\text{CO}_2\text{Et})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , which on hydrolysis gave 4 : 13-*diketopalmitic acid*. This acid is of interest in that, on reduction and dehydration, it should furnish an unsaturated palmitolactone,



which, according to a recent patent (E.P. 292,962 of 1929), has been isolated from female secretory organs, and is claimed to be the physiologically active ovarian hormone.

These statements, in view of the recent remarkable work of Butenandt (compare *Chem.-Ztg.*, 1929, 938) on progynon, must await further confirmation; several authorities have, however, expressed the view that there exists more than one ovarian hormone.

5-*Ketopalmitic acid* has been obtained from lauryl chloride and ethyl sodio- $\alpha$ -acetoglutarate, followed by hydrolysis of the product; the opportunity is taken to describe the 7- and 8-*ketopalmitic acids*, which were obtained by applications of the method of Part I. These substances are the conceivable hydration products of palmitolic acid and have been prepared in connexion with an investigation of the course of that reaction.

#### EXPERIMENTAL.

4-*Ketomyristic Acid*,  $\text{CH}_3\cdot[\text{CH}_2]_9\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ .—Sodium (2.3 g.) was granulated under toluene, washed with ether, and suspended in anhydrous ether (120 c.c.), and ethyl acetosuccinate (21.6 g.) gradually added, the solution of the sodium being completed by heating on the steam-bath for 10 minutes. A solution of undecoyl chloride (obtained from 17.6 g. of the acid by the action of pure thionyl chloride and removal of the excess of the reagent in a vacuum) in ether (20 c.c.) was slowly added to the cooled mixture, which was kept for 12 hours and then refluxed for 10 minutes. The product was isolated and agitated for  $4\frac{1}{2}$  hours with aqueous potassium hydroxide (1200 c.c. of 4%). After acidification with acetic acid and isolation by means of ether, it was submitted to the action of boiling 5% sulphuric acid for 4 hours, and the hydrolysis

was completed by boiling with 8% sodium hydroxide solution for 1 hour. The product crystallised from light petroleum (b. p. 60—80°) in colourless plates (once crystallised; yield, 8.5 g. or 72%), m. p. 87° (Found: C, 69.7; H, 10.7. Calc. for  $C_{14}H_{26}O_3$ : C, 69.4; H, 10.7%) alone or mixed with the specimen previously prepared by another method (Robinson and Robinson, J., 1926, 2204).

$$\begin{array}{c} \text{O} \text{---} \text{CO} \\ | \\ \gamma\text{-n-Decylbutyrolactone, } CH_3 \cdot [CH_2]_9 \cdot CH \cdot CH_2 \cdot CH_2 \end{array}$$

A solution of 4-ketomyristic acid (4 g.) in anhydrous ethyl alcohol (90 g.) was gradually added to sodium (7.5 g.) contained in a flask heated at 150—160°. After 1½ hours, the alcohol was evaporated, and the residue mixed with dilute hydrochloric acid. The product was collected by means of ether, boiled for 30 minutes with 15% hydrochloric acid (120 c.c.) in order to ensure the formation of the lactone from the hydroxy-acid, washed in ethereal solution with aqueous sodium carbonate, freed from the solvent, and crystallised from light petroleum and later from methyl alcohol; it formed long slender needles, m. p. 30—31° (yield, 2.7 g. or 71%) (Found: C, 74.3; H, 11.3.  $C_{14}H_{26}O_2$  requires C, 74.3; H, 11.5%).

5-Ketopalmitic Acid,  $CH_3 \cdot [CH_2]_{10} \cdot CO \cdot [CH_2]_3 \cdot CO_2H$ .—Ethyl sodio-acetosuccinate dissolved in ether when prepared as described above, but ethyl sodio- $\alpha$ -acetylglutarate separated as a colourless powder and the solution of the sodium was thereby hindered.

The reaction in the present case was carried out in the usual manner, sodium (1.4 g.), ether (140 c.c.), ethyl  $\alpha$ -acetylglutarate (13.9 g.), and lauryl chloride (13.0 g.) being used; finally, the mixture was refluxed for 1 hour and the product isolated and shaken with 3% sodium hydroxide solution (850 c.c.) for 12 hours. The mixture was then concentrated on the steam-bath for 1 hour and the acid obtained by addition to ice and hydrochloric acid was crystallised from light petroleum, methyl alcohol and benzene, forming colourless plates, m. p. 88° (Found: C, 71.2; H, 11.2.  $C_{16}H_{30}O_3$  requires C, 71.1; H, 11.1%). On reduction by means of sodium and absolute ethyl alcohol, and treatment of the product with boiling 15% hydrochloric acid, 5-ketopalmitic acid furnished 8-undecylvalerolactone, which crystallised from light petroleum in plates, m. p. 29.5—30.0° (Found: C, 75.5; H, 11.8.  $C_{16}H_{30}O_2$  requires C, 75.6; H, 11.8%).

7-Ketopalmitic Acid,  $CH_3 \cdot [CH_2]_3 \cdot CO \cdot [CH_2]_5 \cdot CO_2H$ .—The condensation product from ethyl sodio- $\alpha$ -acetodecoate (16.5 g. of the ester) and 6-carbethoxyhexoyl chloride (13 g.), prepared in ethereal solution, was isolated and hydrolysed successively by agitation for 5 hours with 3% potassium hydroxide solution (700 c.c.), by boiling with 5% sulphuric acid (500 c.c.) for 24 hours, and, after steam-

distillation for the separation of methyl *n*-nonyl ketone, by boiling with 3½% potassium hydroxide solution for 6 hours. The acid, purified through its sparingly soluble sodium salt (4 g., or 22%) and then by crystallisation from light petroleum and from methyl alcohol, formed colourless plates, m. p. 78° (Found: C, 71·2; H, 11·0.  $C_{16}H_{30}O_3$  requires C, 71·1; H, 11·1%).

*8-Ketopalmitic Acid*,  $CH_3 \cdot [CH_2]_7 \cdot CO \cdot [CH_2]_6 \cdot CO_2H$ .—By an application of the method of Grün and Wirth (*Ber.*, 1922, 55, 2207) for the preparation of ethyl hydrogen sebacate, ethyl suberate (96 g.) gave ethyl hydrogen suberate (49 g.), which furnished 7-carbethoxyheptoyl chloride, b. p. 182°/69 mm. (yield, 85%).

The product from the interaction of ethyl sodio-2-acetononoate (22·8 g. of the ester) and 7-carbethoxyheptoyl chloride (22·2 g.) in dry ether was hydrolysed successively by shaking with 5% potassium hydroxide solution (400 c.c.) for 20 hours, by boiling with 5% sulphuric acid (400 c.c.) for 24 hours, and, after steam distillation, by boiling with 5% sodium hydroxide solution (250 c.c.) for 24 hours. The sodium salt, which separated on cooling, was decomposed; the acid crystallised from methyl alcohol (yield, 5 g. or 18%) in plates, m. p. 77—78° (Found: C, 70·8; H, 11·2.  $C_{16}H_{30}O_3$  requires C, 71·1; H, 11·1%). The oily oxime was converted by sulphuric acid into an amide, m. p. 58°.

The hydration of palmitic acid should yield a mixture of 7- and 8-ketopalmitic acids in which the latter should preponderate, for the reasons explained in Part II (*J.*, 1926, 2205).

The action of sulphuric acid, followed by that of water, on palmitic acid has been studied by Bodenstein (*Ber.*, 1894, 27, 3400), who obtained a ketopalmitic acid, m. p. 74°, the oily oxime of which yielded, on transposition, an amide, m. p. 57·5—58°.

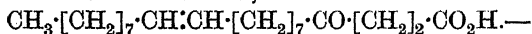
The freezing points of mixtures of 8-ketopalmitic acid and 7-ketopalmitic acid have been determined, and will be published in detail in connexion with a record of experiments on the hydration of palmitic acid. It may be mentioned, however, that the freezing point of a mixture containing 30% of 7-ketopalmitic acid is about 6° lower than that of pure 8-ketopalmitic acid. Since it is certain that the 8-ketopalmitic acid is the major product of the hydration of palmitic acid, it is apparent that the acid obtained by Bodenstein contained at most 30%, and may have contained as little as 10—20%, of the isomeride.

*4-Keto- $\Delta^{13}$ -tetradecenoic Acid*,  $CH_3 \cdot CH \cdot [CH_2]_8 \cdot CO \cdot [CH_2]_2 \cdot CO_2H$ .—The condensation product from ethyl sodioacetosuccinate (21 g. of the ester) and undecenoyl chloride (19·2 g.) was isolated and hydrolysed successively by agitation with 5% potassium hydroxide solution (1000 c.c.) for 8 hours, by boiling with 5% sulphuric acid

(700 c.c.) for 7 hours, and by boiling with 4½% potassium hydroxide solution for 4 hours. The mixture was acidified and steam-distilled in order to remove a little unchanged undecenoic acid; the residual *acid* crystallised from light petroleum in colourless plates, m. p. 79.5° (yield, 14.8 g. or 55%) (Found: C, 69.6; H, 9.7.  $C_{14}H_{24}O_3$  requires C, 70.0; H, 10.0%).

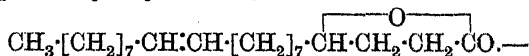
$\gamma$ - $\Delta^9$ -Decenylbutyrolactone was obtained in 89% yield by reducing the acid (6 g.) in anhydrous alcohol (150 g.) with sodium (10 g.) under the usual conditions and subsequent treatment with boiling 15% hydrochloric acid. The lactone crystallised from light petroleum in needles, m. p. 26–27° (Found: C, 74.8; H, 10.7.  $C_{14}H_{24}O_2$  requires C, 75.0; H, 10.7%). A solution in chloroform absorbed bromine, and this lactone is quite different from the decylbutyrolactone previously described.

*trans*-4-Keto- $\Delta^{12}$ -heneicosenoic Acid,



Elaidyl chloride (30.2 g.) and ethyl sodioacetosuccinate (from 21.6 g. of the ester) were brought into reaction in ethereal solution (200 c.c.) in the usual manner and after 12 hours the mixture was boiled for 20 minutes. The product was agitated with 3% potassium hydroxide solution (1000 c.c.) for 8 hours and, after the addition of 30% aqueous potassium hydroxide (25 c.c.), the mixture was boiled for 2 hours. The solid obtained on acidification was crystallised from light petroleum (b. p. 40–60°); after further purification through the sparingly soluble sodium salt and by crystallisation from light petroleum and then from methyl alcohol, the *acid* formed lustrous plates, m. p. 82.5° (yield, 49%) (Found: C, 74.4; H, 11.1.  $C_{21}H_{38}O_3$  requires C, 74.6; H, 11.2%).

$\gamma$ - $\Delta^8$ -Heptadecenylbutyrolactone,

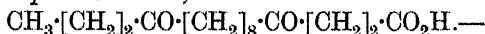


The foregoing acid (9.8 g.), dissolved in absolute alcohol (200 g.), was added in the course of 15 minutes to sodium (15 g.) heated in an oil-bath at 140–150°. The sodium disappeared after 1 hour, and the product was isolated and boiled for 1 hour with 15% hydrochloric acid (180 c.c.). After being washed in ethereal solution with aqueous sodium carbonate, the crude *lactone* was washed with a little light petroleum; it then crystallised from this solvent (b. p. 40–60°) in colourless plates, m. p. 42° (yield, 6.1 g. or 65%) (Found: C, 78.4; H, 11.9.  $C_{21}H_{38}O_2$  requires C, 78.3; H, 11.8%). The unsaturated nature of this substance was confirmed by noting its absorption of bromine in chloroform solution.

10-Ketotridecoic Acid,  $CH_3 \cdot [CH_2]_2 \cdot CO \cdot [CH_2]_8 \cdot CO_2H$ .—Ethyl sodio-2-acetobutyrate (from 31.6 g. of the ester) was prepared in dry ether

(250 c.c.), and 9-carbethoxynonyl chloride (46 g.) gradually added to the solution, which was kept for 12 hours and then refluxed for 20 minutes. The product was hydrolysed in the usual manner with cold 4% potassium hydroxide solution, boiling 6% sulphuric acid, and finally boiling 4% potassium hydroxide solution. The *keto-acid* was separated from sebacic acid by crystallisation from light petroleum, but this was a tedious operation and the yield was poor. The white plates had m. p. 63° (Found: C, 68.6; H, 10.4.  $C_{13}H_{24}O_3$  requires C, 68.4; H, 10.5%).

4 : 13-Diketopalmitic Acid,



10-Ketotridecoic acid (4 g.) was converted into its chloride by the action of thionyl chloride at 60°; decomposition occurred if the temperature was raised; the excess of reagent was removed in a vacuum. The interaction of the chloride with ethyl sodioacetosuccinate (4 g. of the ester) was carried out in the usual manner in dry ethereal solution, and the product was hydrolysed by shaking it for 12 hours with 3% aqueous potassium hydroxide (400 c.c.) and then concentrating the solution on the steam-bath for 1 hour. The *acid* precipitated on acidification crystallised from light petroleum, and then from ethyl acetate, in plates, m. p. 101° (Found: C, 67.7; H, 9.8.  $C_{16}H_{28}O_4$  requires C, 67.6; H, 9.9%).

*β-Benzoylpropionic Acid.*—The applicability of the general method was further confirmed by the preparation of this acid by the usual procedure. The product from ethyl sodioacetosuccinate (12.5 g. of the ester) and benzoyl chloride (8.8 g.) was hydrolysed by cold 1½% aqueous potassium hydroxide (1200 c.c.) for 24 hours, and the solution concentrated on the steam-bath to about 100 c.c. The mixed acids were regenerated and collected and benzoic acid was removed by sublimation at 100°. The residue (4 g.), crystallised from benzene, had m. p. 116°, alone or mixed with a specimen prepared by the action of aluminium chloride on a mixture of benzene and succinic anhydride.

The author wishes to thank Professor R. Robinson for his interest in this investigation.

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CII.—*The Constitution of Carthamin. Part I.*

By (Miss) CHIKA KURODA.

CARTHAMIN, the red colouring matter of safflower, was formerly an important dye, and although the demand for it has declined considerably since the advent of artificial colouring matters, the safflower is still cultivated on a large scale, especially in India and China. Notwithstanding its high cost, carthamin is much appreciated in Japan for certain purposes : it is believed to have remarkable medicinal properties.

Malin (*Annalen*, 1840, 36, 117), Preiser (*J. pr. Chem.*, 1844, 32, 142), Schlieper (*Annalen*, 1846, 58, 357), Radcliffe (*J. Soc. Dyers and Col.*, 1897, 13, 158), and Kametaka (*J. Chem. Soc. Tokyo*, 1906, 27, 1202) investigated carthamin, but Kametaka and Perkin (*J.*, 1910, 97, 1415) were the first to isolate it in a pure crystalline condition. Both Preiser and Radcliffe, the latter using methyl alcohol as solvent, claimed to have isolated carthamin in a crystalline form; their descriptions, however, are somewhat contradictory. Kametaka and Perkin found methyl alcohol unsatisfactory as a solvent and obtained crystalline carthamin by using pyridine : they gave it the provisional formula  $C_{25}H_{24}O_{12}$  and obtained *p*-hydroxybenzoic acid (this was first isolated by Malin), *p*-coumaric acid, *p*-hydroxybenzaldehyde, and picric acid from it by various means, but were unable to prepare crystalline derivatives by methylation, benzylation, or acetylation; carthamin, however, gave crystalline additive compounds with aniline and with  $\beta$ -naphthylamine.

The author began an investigation of carthamin in 1924, but owing to the outbreak of civil war in China the supply of the raw material failed. During the last two years, supplies have again been available, and the author is also deeply indebted to Dr. Kametaka, who provided her with material collected in China by Dr. Momoji Yamazaki.

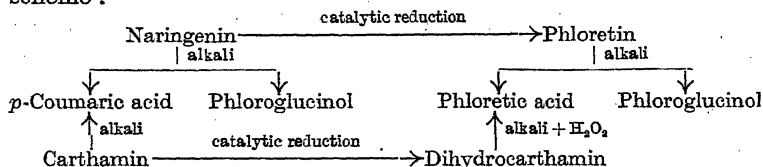
The initial substance used in the present work was a paste (sold as carthamin paste) prepared from the raw material by the traditional method of Japanese manufacturers. The paste was submitted to filtration, and the residue quickly dried on porous tile. The product, when crystallised, with great loss, from pure pyridine by a modification of Kametaka and Perkin's method (*loc. cit.*), gave carthamin, although not in a pure condition. When, however, the dried product was digested with cold dilute hydrochloric acid and again dried, it was converted into a crystalline substance which could be recrystallised from dilute methyl alcohol in good yield,

giving fine, yellow, hydrated needles, m. p. about 228° (decomp.; colour change at about 168°) (Schlieper, *loc. cit.*, obtained from a methyl-alcoholic extract of commercial carthamin a yellow substance, though not in a crystalline form, m. p. about 168°). When the yellow needles were recrystallised from pyridine, a substance separated in red needles with a green iridescence, like those of carthamin obtained by Kametaka and Perkin. Many facts indicate that the red and the yellow substance are isomeric. The latter, named *isocarthamin*, gave analytical results corresponding to the formula  $C_{21}H_{22}O_{11} \cdot 2H_2O$  when freshly prepared and quickly dried, to  $C_{21}H_{22}O_{11}$  after being dried at 60° under reduced pressure, and to  $C_{21}H_{20}O_{10}$  ( $C_{21}H_{22}O_{11} - H_2O$ ) after being dried at 100° under reduced pressure. The last formula also agrees with the analytical data recorded by Kametaka and Perkin (*loc. cit.*, p. 1418).

Carthamin and *isocarthamin* are glucosides. They can be hydrolysed by dilute sulphuric or hydrochloric acid or by emulsin, yielding glucose (1 mol.), but only when the hydrolysis is effected with dilute phosphoric acid can the other components of the glucosides, namely, *carthamidin* and *isocarthamidin*, be ultimately obtained in the crystalline condition. These two substances are separable by means of moist chloroform, in which *isocarthamidin* is insoluble and *carthamidin* is slightly soluble. The latter separates from the solution in pale yellow, hydrated needles,  $C_{15}H_{12}O_6 \cdot H_2O$ , m. p. 218°. *isoCarthamidin* separates from dilute methyl alcohol in yellow, hydrated, rhombic crystals, m. p. 240°, which lose water at 100° under reduced pressure.

Carthamidin and *isocarthamidin* have phenolic properties: they can be acetylated, but are inert towards methyl iodide, methyl sulphate, and diazomethane. When they are reduced in methyl-alcoholic solution with magnesium and hydrochloric acid, they give a magenta coloration, resembling in this respect a flavonol such as quercetin. Their absorption spectra, however, differ from those of the flavonols, and also, on decomposition by alkali, they behave somewhat differently from quercetin in that they easily yield *p*-hydroxybenzaldehyde and *p*-coumaric acid, whereas quercetin under the same conditions gives, not the corresponding aldehyde, but protocatechuic acid. It is interesting that naringin (the glucoside of naringenin), until recently considered to be a hydroxychalcone derivative, develops a red coloration on treatment in methyl-alcoholic solution with magnesium and hydrochloric acid (Tsujimura, *Bull. Inst. Phys. Chem. Res. Tokyo*, Vol. VI, 12, 1111). On the other hand, phloretin, which is closely related to naringenin, gives on treatment with alkali the products mentioned below (Will, *Ber.*, 1885, 18, 1322; Michael, *Ber.*, 1894, 27, 2687;

Sonn, *Ber.*, 1913, 46, 4050; Franck, *Centr.*, 1914, II, 253). Dihydrocarthamin (IX), obtained from carthamin by catalytic reduction, gives phloretic acid when treated with hydrogen peroxide in alkali-carbonate solution. These relationships are shown in the following scheme:



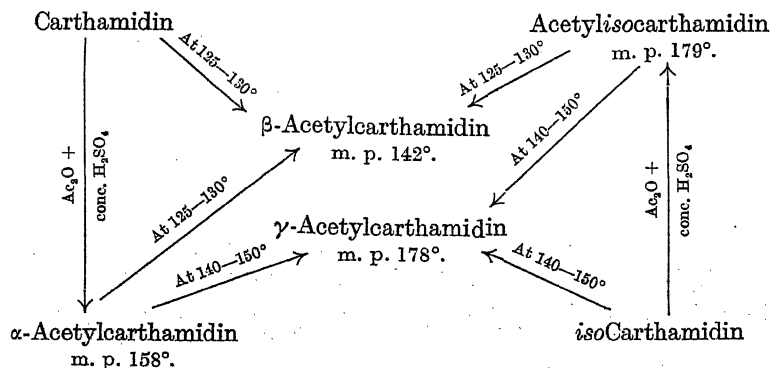
The author has so far been unable to prepare a polyhydroxybenzene from carthamin and its derivatives: only monohydric phenols such as *p*-hydroxybenzaldehyde, tribromophenol, and *p*-hydroxybenzoic, *p*-coumaric, phloretic, and picric acids—and these in poor yield—have been obtained. The following reactions of carthamidin and isocarthamidin, however, indicate, not only the presence of a polyhydroxybenzene nucleus, but also, when compared with similar reactions of di- and tri-hydric phenols of known constitutions (see table on p. 761), the relative positions of the hydroxyl groups. (1) Ferric chloride in methyl-alcoholic solution produces a transient bluish-green coloration, changing to purple-brown, and finally a brown precipitate (compare quinol). (2) An aqueous solution of barium hydroxide gives a bright indigo-blue colour (a precipitate from concentrated solutions) and then a reddish-brown precipitate: this is a very delicate test. (3) Lead acetate in methyl-alcoholic solution produces a yellow precipitate which becomes brown and then bluish-green or dark green. (4) When carthamidin is rubbed on a watch-glass with a rod moistened with 2*N*-sodium hydroxide, it becomes blue and then reddish-brown (isocarthamidin does not give this test).

When the tests (1), (2), and (3) were applied to the di- and tri-hydric phenols of known constitutions, the relative positions of the hydroxyl groups were distinguishable in the following manner: (1) if two hydroxyls are in the ortho-position with respect to each other, precipitation occurs in all three tests; (2) if there are two hydroxyls in the para-position with respect to each other, the substance gives a delicate colour change. Quinol and 2:4-dihydroxy-1:3-dimethoxybenzene resemble carthamidin in their colour reactions in test (4).

In view of these results, it is concluded that reactions (1), (2), and (3) show that hydroxyl groups in carthamidin must be arranged as those in hydroxyquinol, *viz.*, one pair in the ortho relation, and another pair in the para relation, to each other. These two sub-



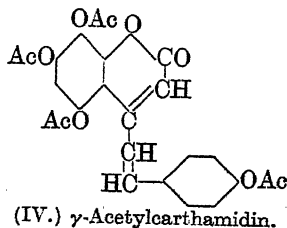
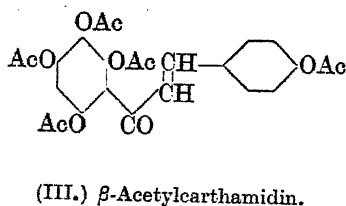
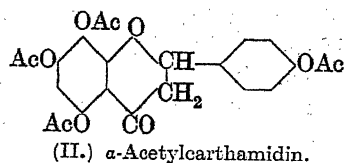
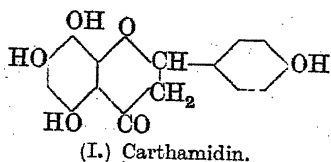
stances are also alike in their instability towards boiling water and on exposure to air. Numerous attempts were made to produce a polyhydroxybenzene from carthamin, *isocarthamin*, and carthamidin by very cautiously decomposing them with hot aqueous barium hydroxide in an atmosphere of hydrogen; however, only *p*-coumaric acid, *p*-hydroxybenzaldehyde, and an acid which appeared to be gluconic acid were isolated. The hydroxylated nucleus of carthamidin is therefore much more unstable than hydroxyquinol. Now, 1:2:3:5-tetrahydroxybenzene is so unstable that it is decomposed by boiling water, and its colour reaction with alkali given in the literature resembles reaction (4) of carthamidin. If, then, this is the hydroxylated nucleus of carthamidin, the reactions described above and also the results of acetylating carthamidin and *isocarthamidin* under various conditions (see below) become explicable.



(For the reactions where no reagent is indicated, a mixture of sodium acetate and acetic anhydride was used.)

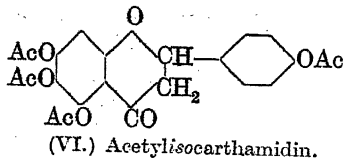
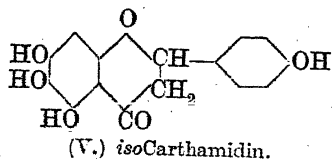
Shortly after reaching the above conclusion regarding the constitution of carthamin the author discovered that Chapman, Perkin, and Robinson (J., 1927, 3015) had shown that carajurin gave no appreciable quantity of polyhydric phenol on decomposition with alkali—a fact which in their opinion supported rather than discredited the constitution of a tetrahydroxybenzene derivative assigned to the substance. Hence it is concluded that carthamidin and *isocarthamidin* are hydroxychalcone derivatives. It is in general difficult to distinguish hydroxychalcones from hydroxyflavanones owing to their easy interconvertibility. According to Asahina, Shinoda, and Inubuse (*J. Pharm. Soc. Japan*, 1928, 48, 208, 868) the colour reaction (2) above is negative for hydroxychalcones but positive for hydroxyflavanones, and on this ground

naringin and other similar substances were shown to be hydroxy-flavanones. Hence it follows that carthamidin also belongs to this class of substance. The colour reaction (2) is also given by *isocarthamidin*,  $\alpha$ -acetylcarthamidin, and *acetylisocarthamidin*, but not by  $\beta$ - and  $\gamma$ -acetylcarthamidin.  $\beta$ -Acetylcarthamidin is a penta-acetyl derivative and  $\alpha$ -acetylcarthamidin and *acetylisocarthamidin* are tetra-acetyl derivatives. The analytical results are in complete accord with the following formulations of carthamidin and its acetyl derivatives.



When rubbed with alkali [colour reaction (4) above], *isocarthamidin* behaves like pyrogallol in that both turn brown without previously becoming indigo-blue; 1:2:3:5-tetrahydroxybenzene behaves like carthamidin; and pyrocatechol becomes indigo-blue, the colour being fairly persistent.

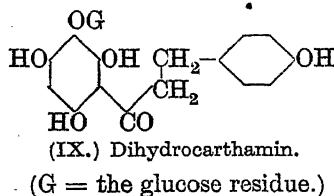
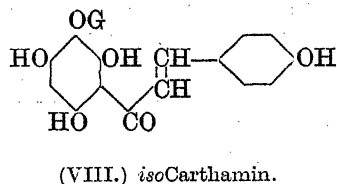
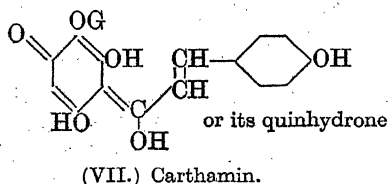
The structures of *isocarthamidin* and *acetylisocarthamidin* are probably (V) and (VI) respectively.



The constitutional change from a flavanone (I, II, V, VI) into a chalcone (III) or into a coumarin derivative (IV) which accompanies the acetylation finds support in the analogies furnished by naringenin (Asahina, Shinoda, and Inubuse, *loc. cit.*) for the former change and by phloretin and maulurin (Ber., 1895, 28, 1393) for the latter change. Moreover, the absorption spectrum of  $\beta$ -acetylcarthamidin (III) resembles that of chalcone (phenyl styryl ketone)

itself very closely, whereas the spectra of carthaminidin and *iso*-carthaminidin resemble the spectrum of naringin.

The glucosides carthamin and *isocarthamin* are considered to have the formulæ (VII) and (VIII) respectively (they may also be *cis*- and *trans*- isomerides), because by means of reactions (2) and (3) it can be shown that neither contains two hydroxyls in the ortho-relation and hence it is probable that the glucose residue is in the position indicated. Moreover, the glucosides yield *p*-hydroxybenzaldehyde very easily, whereas the components carthaminidin and *isocarthaminidin* do not under the same conditions. The difficulty of obtaining carthaminidin from dihydrocarthamin may be explained by representing the latter by the formula (IX).



The investigation is being continued.

#### EXPERIMENTAL.

*Preparation of Carthamin.*—The filtered dried product (20–25 g.) obtained from commercial carthamin paste (1 kg.) was in quantities of 5 g. extracted several times with pyridine (200 c.c. in all) on a water-bath; the insoluble material was 25–30% of the whole. The extracts were concentrated under reduced pressure to small bulk, water was added, and the fine red needles that slowly formed were collected and washed with acetone (yield, 2–3 g.). The sample for analysis was submitted to the above purification at least three times and was then warmed with acetone and ether and dried at 100° under reduced pressure. The analytical results, the melting point, and other properties agreed with those recorded by Kametaka and Perkin (*loc. cit.*) and the substance was identical with a specimen of carthamin kindly supplied by Dr. Kametaka (Found: C, 58.8, 57.8; H, 4.9, 4.8; ash, trace. Calc. for  $C_{21}H_{20}O_{10}$ : C, 58.2; H, 4.6%).

Each crystallisation from pyridine caused the loss of almost half of the carthamin; some of this was recovered by acidifying the fresh mother-liquor with sulphuric acid at  $0^{\circ}$ .

*Preparation of isoCarthamin.*—Crude carthamin (5 g.) was digested with water (100 c.c.) and 12% hydrochloric acid (15 c.c.) and after several hours the solid was collected, washed with water and dried on tile (yield, about 4.5 g. There was no loss when purified carthamin was used in the digestion). When a little water was added to a hot methyl-alcoholic solution of the product, *iso-carthamin* gradually separated in yellow needles (yield, about 50%); these were collected and dried quickly by washing with methyl alcohol and then with ether; m. p.  $228^{\circ}$  (reddening at about  $168^{\circ}$ ) (Found: C, 52.1, 52.0; H, 5.1, 5.2.  $C_{21}H_{22}O_{11} \cdot 2H_2O$  requires C, 51.9; H, 5.3%. Found in material dried at  $60^{\circ}$  under reduced pressure: C, 55.7; H, 4.9.  $C_{21}H_{22}O_{11}$  requires C, 56.0; H, 4.9%). When *isocarthamin* was heated at  $100^{\circ}$  under reduced pressure, it changed into a brown substance resembling that obtained from carthamin under the same conditions (Found: C, 57.9; H, 4.8. Calc. for  $C_{21}H_{20}O_{10}$ : C, 58.2; H, 4.6%).

*isoCarthamin* could not be obtained crystalline from ethyl-alcoholic solution, nor from methyl alcohol if the solution was concentrated by distillation, even under reduced pressure: in order to recover *isocarthamin* from such spoiled solutions, repetition of the treatment with hydrochloric acid is necessary. The yellow crystals of *isocarthamin* are stable in a sealed tube, but change to a red powder on exposure to air. *isoCarthamin* is soluble in water, but the yellow solution, on standing or when boiled, becomes pink in the same way as an aqueous solution of carthamin.

*Decomposition of Carthamin or isoCarthamin with Hot Dilute Hydrochloric Acid.*—When either substance was heated with 7% hydrochloric acid for 20 minutes, it changed into a black amorphous powder. The aqueous solution (1) yielded nothing crystalline to ether, (2) reduced Fehling's solution, (3) gave no immediate precipitate when treated with phenylhydrazine, the absence of mannose thus being indicated, (4) gave no results when tested for gluconic acid and pentoses by means of naphtharesorcinol and phloroglucinol respectively.

*Glucosazone from Carthamin or isoCarthamin.*—A mixture of 12% hydrochloric acid (5 c.c.), *isocarthamin* (or carthamin) (0.55 g.), and water (5 c.c.) was heated on a water-bath for 1 hour, and the black product was washed with water. The filtrate and washings were neutralised with sodium carbonate, concentrated on a water-bath, and warmed with sodium acetate (0.57 g.) and phenylhydrazine hydrochloride (0.38 g.). Glucosazone, which separated

very slowly, after being washed and dried (yield, 0.055 g.), melted at  $206^{\circ}$ , alone or mixed with an authentic specimen (Found: C, 60.2; H, 6.1. Calc.: C, 60.3; H, 6.2%).

*Determination of glucose.* In a similar experiment (*isocarthamin*, 0.2043 g.; water, 4 c.c.; 12% hydrochloric acid, 6 c.c.) the neutralised filtrate and washings were diluted to 100 c.c. with 10% aqueous ammonia and the glucose in the solution was estimated by Pavy's volumetric method (Found:  $C_6H_{12}O_6$ , 37.0, 36.9.  $C_{21}H_{22}O_{11} \cdot 2H_2O$  requires  $C_6H_{12}O_6$ , 37.0%). The same result was obtained with carthamin.

*Optical rotation of the sugar solution.* *isoCarthamin* (0.6 g.), water (6 c.c.), and 12% hydrochloric acid (9 c.c.) were heated together as before, the aqueous solution was made up to 20 c.c. (it was assumed to be a 1.1% glucose solution), and the rotation was observed:  $[\alpha]_D^{25} + 53^{\circ}$  (calc.,  $+ 52.6^{\circ}$ ). The author wishes to thank Mrs. Okada and Miss Yamaguchi for their help in this experiment.

*Catalytic Reduction of Carthamin.*—Carthamin (0.2 g.), suspended in ethyl alcohol (25 c.c.), was treated with hydrogen in the presence of palladium-black. The volume of the gas diminished during the first 10 minutes, then increased fairly rapidly to the original value, and thereafter remained almost constant. The carthamin gradually dissolved, giving a yellow solution. After 4–5 hours, the solvent was evaporated at the ordinary temperature and the residue, freed from the palladium, was kept in contact with a little water in an open vessel: fine yellow needles (probably hydrated) separated; they were insoluble in benzene and chloroform, fairly readily soluble in acetone, and very soluble in methyl alcohol (yield, about 70%). The crystals became red on drying in a desiccator, but yellow again on exposure to the air. The combustion of the substance was sluggish, requiring 2 hours for completion even on the micro-scale (Found in material dried at  $90^{\circ}$  under reduced pressure: C, 55.0; H, 5.5.  $C_{21}H_{24}O_{11}$  requires C, 55.6; H, 5.3%), but the behaviour of the product on decomposition with alkali and hydrogen peroxide (see p. 763) convinced the author that it was actually *dihydro-carthamin*.

*Decomposition of Carthamin or isoCarthamin with Phosphoric Acid.*—The powdered material (5 g.) was heated with a 9% aqueous solution of phosphoric acid (100 c.c.) on a water-bath for 40 minutes in a closed vessel, carbon dioxide being passed during the whole time. The liquid was filtered hot, cooled, extracted repeatedly with ether, and used again to decompose more of the residual solid: after four repetitions, only a small quantity of a black solid remained. The combined ethereal extracts were evaporated, leaving a residue which, after addition of a very little aqueous

acetone, slowly solidified to a yellow crystalline cake (yield, about 30%). Subsequently it was found that the dry raw material obtained directly from the original carthamin paste may be used for the preparation of the same substance in good yield (about 15% of the raw material).

*Isolation of carthamidin (I).* The crystalline cake (above) was warmed with successive quantities of moist chloroform for a few minutes, until nothing crystallised from the rapidly filtered extract on cooling. *Carthamidin* was thus obtained in pale yellow needles containing one molecule of water (yield, 30% of the crude product), and sometimes also in long needles on repetition of the purification; m. p. 218° (Found: C, 58.8, 58.9; H, 4.8, 4.4.  $C_{15}H_{12}O_6 \cdot H_2O$  requires C, 58.8; H, 4.6%. Found in material heated at 100° under reduced pressure: C, 62.7; H, 4.4; *M*, ebullioscopic in acetone, 298, 286, 270.\*  $C_{15}H_{12}O_6$  requires C, 62.5; H, 4.2%; *M*, 288).

*Carthamidin* is very soluble in acetone, methyl alcohol, acetic acid, and ethyl acetate, but sparingly soluble in light petroleum, benzene, dry chloroform, and cold water. It crystallises from hot aqueous solution in the hydrated form, but is decomposed by prolonged boiling: even at the ordinary temperature it seems to decompose slowly in aqueous solution.

When carthamin or *isocarthamin* was heated with 1% sulphuric or hydrochloric acid, no trace of *carthamidin* or *isocarthamidin* was produced.

*isocarthamidin (V).* The residue left after the extraction of the *carthamidin* with moist chloroform was dissolved in the minimum quantity of acetone: on addition of chloroform (3—4 vols.), *isocarthamidin* remained in solution but a dark resinous substance was precipitated. The latter was repeatedly dissolved in acetone and reprecipitated with chloroform. When the combined filtrates were allowed to evaporate to dryness, somewhat rounded crystals were produced; these were washed with ether and recrystallised twice from dilute methyl alcohol, *isocarthamidin* being obtained in yellow hydrated prisms, m. p. 240° (Found in material dried at 100° under reduced pressure: C, 62.5; H, 4.3.  $C_{15}H_{12}O_6$  requires C, 62.5; H, 4.2%).

When dihydrocarthamin was treated with dilute phosphoric acid under the same conditions as carthamin, no crystalline product was obtained.

*Carthamidin* and *isocarthamidin* resemble each other very closely in many of their properties. The former seems to be converted into the latter under certain conditions; for instance, when it is

\* The author is indebted to Mr. Shiba for carrying out these determinations of molecular weight.

heated with water in air or in a sealed tube at 100° or higher or with animal charcoal at 100° in aqueous solution.

*Reactions of Phenols* (see p. 754).—A = ferric chloride in methyl-alcoholic solution; B = lead acetate in methyl-alcoholic solution; C = barium hydroxide in aqueous solution.

	A.	B.	C.
Resorcinol	No ppte.	No ppte.	No change
Phloroglucinol	"	"	"
Pyrocatechol	Blue → green ppte.	Ppte.	Light blue → white ppte.
Pyrogallol	Green → brown ppte.	"	Violet-brown ppte.
Quinol	Blue → brown ppte.	No ppte.	Yellowish-brown ppte.
Hydroxyquinol	Reddish-brown	Ppte.	Reddish-brown ppte.
2 : 4-Dihydroxybenzoic acid	Violet	No ppte.	No change
3 : 4-Dihydroxybenzoic acid	Green	White ppte.	Light blue → white ppte.
2 : 5-Dihydroxybenzoic acid	Blue	No ppte.	No change
3 : 4 : 5-Trihydroxybenzoic acid	Blue ppte.	White ppte.	Blue ppte.
3 : 4 : 5-Trihydroxyacetophenone	Violet	Yellow ppte.	Violet ppte.

*α-Acetylcarthamidin* (II).—When carthamidin (0.1 g.), suspended in acetic anhydride (1 c.c.), was cooled and treated with a trace of concentrated sulphuric acid, reaction started immediately with evolution of heat. After several hours, water was added and the precipitate, which separated slowly, was collected, washed with water, and dried (yield, almost theoretical). This *acetyl* compound crystallised from methyl alcohol in colourless prisms, m. p. 158° [Found: C, 60.5, 60.3; H, 4.5, 4.4;  $\text{CH}_3\cdot\text{CO}$ , determined by Freudenberg's method (*Annalen*, 1923, **433**, 230), 36.4, 36.6; *M*, ebullioscopic in benzene, 425, 445, 470.  $\text{C}_{15}\text{H}_8\text{O}_6(\text{CH}_3\cdot\text{CO})_4$  requires C, 60.5; H, 4.4;  $\text{CH}_3\cdot\text{CO}$ , 37.7%; *M*, 456]. It was very easily soluble in chloroform, benzene and acetone, fairly readily soluble in ether and methyl alcohol, and difficultly soluble in water. A methyl-alcoholic solution gave (1) no colour with ferric chloride, (2) a magenta colour (slowly) on reduction with magnesium and hydrochloric acid. When heated with hydrochloric acid in methyl-alcoholic solution, the acetyl derivative gave carthamidin, which was identified by its m. p. after being washed with ether to remove a red impurity. Acetylcarthamidin was optically inactive in benzene solution.

*Acetylisocarthamidin* (VI).—This was prepared in almost theoretical yield in the same way as *α-acetylcarthamidin*. It is easily soluble in benzene, chloroform, and acetone, sparingly soluble in

methyl alcohol, and almost insoluble in ether. When ether or methyl alcohol is added to its chloroform solution, *acetylisocarthamidin* separates in fine, colourless, silky needles, m. p. 179° [Found: C, 60.5, 60.4; H, 4.5, 4.4;  $\text{CH}_3\cdot\text{CO}$ , 37.4; *M*, ebullioscopic in benzene, 430, 442.  $\text{C}_{15}\text{H}_8\text{O}_6(\text{CH}_3\cdot\text{CO})_4$  requires C, 60.5; H, 4.4;  $\text{CH}_3\cdot\text{CO}$ , 37.7%; *M*, 456].

The absorption spectrum of *acetylisocarthamidin* and its behaviour towards ferric chloride and towards magnesium and hydrochloric acid are the same as those of  $\alpha$ -*acetylcarthamidin*.

The differences in melting point, crystalline form, and solubility in methyl alcohol and in ether of these two acetyl compounds are important as means of identifying *carthamidin* and *isocarthamidin*, which are otherwise difficult to distinguish from each other.

$\beta$ -*Acetylcarthamidin* (III).—A mixture of *carthamidin* (0.1 g.), anhydrous sodium acetate (0.5 g.), and acetic anhydride (1.5 c.c.) was heated at 125–130° for 5 hours; the product was then cooled and mixed with water. After the excess of acetic anhydride had been decomposed, the precipitate was collected, washed with water, and dried (yield, nearly 0.14 g.). It crystallised from methyl alcohol in large rhombs, m. p. 142° [Found: C, 60.3, 60.3; H, 4.5, 4.5;  $\text{CH}_3\cdot\text{CO}$ , 42.7, 42.1.  $\text{C}_{15}\text{H}_7\text{O}_6(\text{CH}_3\cdot\text{CO})_5$  requires C, 60.2; H, 4.4;  $\text{CH}_3\cdot\text{CO}$ , 43.2%].

$\beta$ -*Acetylcarthamidin* in methyl-alcoholic solution gives a colour reaction neither with ferric chloride nor with magnesium and hydrochloric acid. It is very easily soluble in chloroform and acetone and sparingly soluble in cold methyl alcohol and ether. It may also be obtained in almost theoretical yield from *isocarthamidin*,  $\alpha$ -*acetylcarthamidin* and *acetylisocarthamidin* by the same method.

$\gamma$ -*Acetylcarthamidin* (IV).—A mixture of *carthamidin* (0.1 g.), anhydrous sodium acetate (0.5 g.), and acetic anhydride (1.5 c.c.) was heated in an oil-bath at 140–150° for 5 hours: the procedure was then as described above, but a further quantity of the product was obtained from the aqueous filtrate by extraction with ether.  $\gamma$ -*Acetylcarthamidin* separated from methyl alcohol in minute colourless crystals, m. p. 178°. The yield was poor (about 25%), because  $\beta$ -*acetylcarthamidin* and a decomposition product were also formed: these rendered the purification rather tedious (Found: C, 62.5, 62.6; H, 4.3, 4.3.  $\text{C}_{25}\text{H}_{20}\text{O}_{10}$  requires C, 62.5; H, 4.2%). The compound may also be obtained from *isocarthamidin*,  $\alpha$ -*acetylcarthamidin*, and *acetylisocarthamidin* by the above method, though in poor yield.

$\gamma$ -*Acetylcarthamidin* resembles *acetylisocarthamidin* in appearance and their melting points are almost the same. The two sub-



stances, however, differ in solubility in many solvents, particularly methyl alcohol and ether, in each of which the former is the more soluble and dissolves fairly readily. Its methyl-alcoholic solution gives a colour reaction neither with ferric chloride nor with magnesium and hydrochloric acid.

*Action of Hydrogen Peroxide on Carthamin* (compare Kametaka and Perkin, *loc. cit.*).—A solution of carthamin (1 g.) in 1% aqueous sodium carbonate (60 c.c.) and 3% aqueous hydrogen peroxide (40 c.c.) was kept at the ordinary temperature until it became yellow; it was then acidified with dilute sulphuric acid and extracted with ether. The residue after evaporation of the ether was dried, extracted with hot benzene to remove a trace of *p*-hydroxybenzaldehyde, dissolved in hot water, and decolorised with animal charcoal; on cooling, *p*-coumaric acid crystallised (yield, about 10%), m. p. 210° (Found: C, 65.9; H, 4.8. Calc.: C, 65.9; H, 4.9%).

*Action of Hydrogen Peroxide on Quercetin*.—The above operation was applied to quercetin, protocathechuic acid, m. p. 199°, being obtained in theoretical yield (Found: C, 54.3; H, 3.9. Calc.: C, 54.6; H, 3.9%).

*Action of Hydrogen Peroxide on Dihydrocarthamin and on Phloretin*.—Dihydrocarthamin (0.2 g.) was treated in the same way as carthamin (one-fifth quantities). The product obtained after evaporation of the ether was pressed on a tile; the crystalline residue (about 0.03 g.), m. p. about 125°, separated from hot concentrated aqueous solution (animal charcoal) in prisms, m. p. 129° (Found: C, 65.1; H, 6.1. Calc. for  $C_9H_{10}O_3$ : C, 65.1; H, 6.0%).

In a similar way phloretin gave phloretic acid (Found: C, 65.1; H, 5.9%) which, alone or mixed with the specimen obtained from dihydrocarthamin, melted at 129°.

*Action of Bromine Water on Carthamin*.—When digested with bromine water (100 c.c.), carthamin (0.5 g.) yielded a yellow precipitate (about 0.6 g.), decomp. about 146° (Found: C, 26.7; H, 2.5; Br, 53.0%). This substance slowly changed into a brown resin and a small quantity of tribromophenol sublimed. When the substance was heated with 5% aqueous alkali and the acidified product distilled with steam, tribromophenol was obtained.

*Action of Alkali on Carthamin and its Decomposition Products*.—The black amorphous powder produced by the decomposition of carthamin with dilute hydrochloric acid (see p. 758) (4.5 g.) was heated with potassium hydroxide (5 g.) and water (2 c.c.) at 160° for 30 minutes. The bluish-green product, when dissolved in water, became violet and then brown. The solution was acidified with dilute sulphuric acid, the precipitate (0.15 g.) removed, and the

filtrate extracted with ether. From the extract, a substance (0.2 g.) was obtained which gave *p*-hydroxybenzoic acid, m. p. and mixed m. p.  $210^{\circ}$ , on purification (Found : C, 60.8; H, 4.2. Calc. : C, 60.9; H, 4.4%).

Carthamin was heated with 5% aqueous caustic alkali and the solution was then acidified and extracted with ether : *p*-hydroxybenzaldehyde and *p*-coumaric acid were isolated from the extract. When concentrated caustic alkali (about 20%) was used, only *p*-hydroxybenzaldehyde was obtained (compare Kametaka and Perkin, *loc. cit.*). When carthamin was fused with potassium hydroxide and a little water at  $140^{\circ}$ , a bluish-green mass was obtained from which *p*-hydroxybenzoic acid, m. p.  $210^{\circ}$ , was isolated in a yield of nearly 10%. Various concentrations of caustic alkali produced only *p*-hydroxybenzaldehyde from carthamidin or isocarthamidin (even from 0.02 g.).

*Action of Hot Baryta Water on Carthamin.*—Carthamin (3 g.) and hot saturated aqueous baryta (60 c.c.) were heated together on a water-bath for 5 hours in an atmosphere of hydrogen. Carbon dioxide was passed through the cooled liquid, the precipitate removed, and the filtrate extracted with ether : from the extract, *p*-hydroxybenzaldehyde (0.33 g.) was isolated. Dilute sulphuric acid was added to the aqueous liquid, the barium sulphate removed, and the filtrate extracted with ether : from this extract, *p*-coumaric acid (0.24 g.) was isolated. The aqueous liquid was now treated with basic lead acetate and, after filtration, with hydrogen sulphide. After further filtration it was concentrated by distillation under reduced pressure, a colourless, acidic, syrupy residue (about 0.5 g.) being obtained. This substance did not reduce Fehling's solution and gave no colour reaction with ferric chloride. When it was heated, it swelled and charred, emitting an odour resembling that of burning tartaric acid or sugar. The substance, which appeared to be gluconic acid, was neutralised with potassium carbonate and the concentrated aqueous solution was treated with alcohol; the white crystals produced were washed with ether and dried in a desiccator (Found : K, 16.0. Calc. for  $C_6H_{11}O_7K$  : K, 16.7%).

The same process applied to isocarthamin gave the same products, but its application to carthamidin was not successful owing to the insolubility of the barium salt in water.

*Absorption Spectra of Carthamidin, isoCarthamidin,  $\alpha$ -Acetylcarthamidin, Acetylisocarthamidin,  $\gamma$ -Acetylcarthamidin, Chalkone, and Naringin.*—The spectra were photographed through the kindness of Mr. Sakurai. In each case the substance was dissolved in ethyl alcohol and concentrations of  $N/5000$ — $N/10000$  were employed, the iron arc being used as the light source. Carthamidin

and isocarthamidin resemble each other closely and have bands with centres at about  $\lambda$  2900 Å. Both substances cut off the violet end of the visible spectrum to nearly equal extents in  $N/5000$ -solutions. The absorption spectrum of naringin has a general resemblance to that of carthamidin in  $N/10000$ -solution.  $\alpha$ -Acetylcarthamidin and acetylisocarthamidin give similar absorptions, both having shallow bands with centres at about  $\lambda$  2600 Å and transmitting the light rather more freely in the ultra-violet region. The absorption spectra of these two substances differ from that of  $\beta$ -acetylcarthamidin, which, however, resembles that of chalkone to some extent, since it has a band with centre at about  $\lambda$  3000 Å. All the absorption spectra seem to have some sharp narrow bands in the near ultra-violet region, but these are difficult to fix with certainty owing to the strong iron lines in their neighbourhood.

The author desires to thank the Keimeikai Society and the Department of Education for grants and to express her appreciation of the helpful interest shown by Prof. Majima and of the assistance of Miss Inouye and Miss Matsuguma. She also has pleasure in acknowledging her indebtedness to Prof. W. H. Perkin for his valuable assistance in publication, and to Prof. A. G. Perkin for his kind criticism.

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### CIII.—*The Constitution of Carthamin. Part II.* *$\beta$ -Carthamidin Pentamethyl Ether and its Synthesis.*

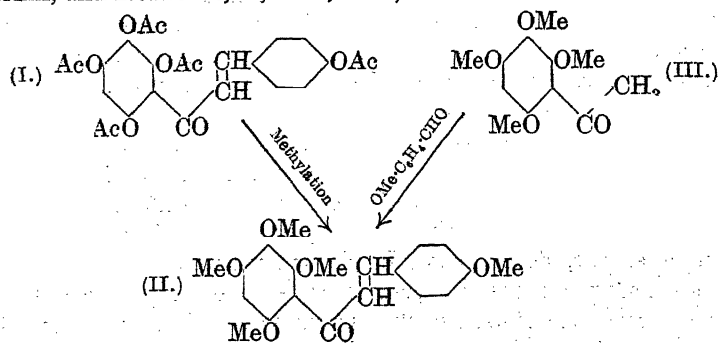
By (Miss) CHIKA KURODA.

ONE of the chief hindrances to the study of carthamin and carthamidin, namely, their resistance to methylation, has now been removed.  $\beta$ -Acetylcarthamidin (I) has been methylated by Freudenberg's method (*Annalen*, 1923, **433**, 236): the product,  $\beta$ -carthamidin pentamethyl ether (II), is identical with synthetic 2:3:4:6-tetramethoxyphenyl 4-methoxystyryl ketone.

Carthamin, therefore, which has long been considered a specially complex colouring matter, is a member of a typical class, the hydroxychalkones: it may, however, assume the quinonoid (see formula VII of the preceding paper) or quinhydrone form.

2:3:4:6-Tetramethoxyacetophenone (III) is produced in almost theoretical yield from 1:2:3:5-tetramethoxybenzene and acetyl chloride in the presence of aluminium chloride but in the absence of a solvent (compare Bargellini and Bini, *Atti R. Accad.*

*Lincoi*, 1910, **19**, 595; Bargellini, *Gazzetta*, 1914, **49**, 47; Chapman, Perkin, and Robinson, *J.*, 1927, 3020).



#### EXPERIMENTAL.

**Methylation of  $\beta$ -Acetylcarthamidin.**—50% Potassium hydroxide solution (7 c.c.) was added with great caution to a solution of methyl sulphate (3 c.c.) and  $\beta$ -acetylcarthamidin (0.2 g.) in methyl alcohol (15 c.c.) in an atmosphere of hydrogen: to complete the reaction, a little heat was supplied. When water was added to the product,  $\beta$ -carthamidin pentamethyl ether (II) separated as a fine precipitate (0.05–0.06 g.). A chloroform solution of the products of several preparations was evaporated and the methyl ether, obtained in prisms, was washed with ether and recrystallised from methyl alcohol; m. p.  $112^\circ$  (Found: C, 66.8; H, 6.0.  $\text{C}_{20}\text{H}_{22}\text{O}_6$  requires C, 67.0; H, 6.1%).

$\beta$ -Carthamidin pentamethyl ether is almost colourless (very pale yellow) and is readily soluble in chloroform and benzene and fairly readily soluble in ether and alcohol; it gives a red solution in concentrated sulphuric acid, and is coloured red by concentrated hydrochloric acid, showing distinct halochromy.

**Synthesis of  $\beta$ -Carthamidin Pentamethyl Ether (2:3:4:6-Tetramethoxyphenyl 4-Methoxystyryl Ketone).**—Pyrogallol trimethyl ether was obtained by Chapman, Perkin, and Robinson's method (*J.*, 1927; 3028), the yield being much improved (26.3 g.; m. p.  $47^\circ$ ) when the following quantities were used: pyrogallol 20 g., methyl alcohol 50 c.c., methyl sulphate 45 c.c., 40% sodium hydroxide solution 90 c.c. It was converted by Graebe and Hess's method (*Annalen*, 1905, **340**, 237) into 2:6-dimethoxybenzoquinone, which gave 2:6-dimethoxyquinol on reduction with sulphurous acid. The product was treated with benzene, which removed a nitrated impurity.

When a crystal of 2:6-dimethoxyquinol is touched with 2*N*-caustic alkali on a watch-glass, an intense indigo-blue colour is produced which immediately changes to brown.

1 : 2 : 3 : 5-Tetramethoxybenzene (2.1 g.; m. p.  $47^{\circ}$ ) was obtained when a mixture of 2 : 6-dimethoxyquinol (2 g.), methyl alcohol (5 c.c.), and methyl sulphate (5.2 c.c.) was treated with 40% sodium hydroxide solution (15 c.c.) in an atmosphere of hydrogen, a little heat being finally supplied.

A mixture of the tetramethoxybenzene (2 g.) and acetyl chloride (4 c.c.), cooled in water, was gradually treated with powdered aluminium chloride (2 g.). When the product became semi-solid (after 20 minutes), ice was added; 2 : 3 : 4 : 6-tetramethoxyacetophenone (2.2 g.) then crystallised in colourless needles. These were collected, digested with aqueous caustic alkali (which removed only a trace of demethylated material), and washed with water (yield, 2.1—2.2 g.). When much water was added to its concentrated methyl-alcoholic solution, the ketone separated in long fine needles (Found: C, 60.1; H, 6.4; OMe, 51.1. Calc.: C, 60.0; H, 6.6; OMe, 51.7%). The *oxime*, prepared by heating a mixture of the ketone (0.3 g.), sodium acetate (0.25 g.), hydroxylamine hydrochloride (0.25 g.), and ethyl alcohol (4 c.c.) on a water-bath for 3 hours, crystallised from dilute methyl alcohol in colourless hydrated needles, m. p.  $53-54^{\circ}$  (Found: C, 53.1; H, 7.0.  $C_{12}H_{17}O_6N, H_2O$  requires C, 52.8; H, 7.0%).

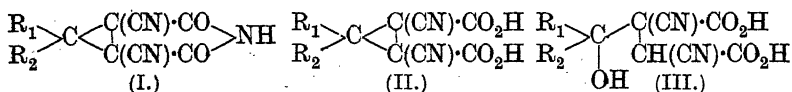
When a solution of the tetramethoxyacetophenone (1 g.) and anisaldehyde (0.7 g.) in methyl alcohol (6 c.c.) was warmed at  $50-60^{\circ}$  with 50% potassium hydroxide solution (4 g.), the methoxy-chalkone gradually crystallised. After several hours, water was added and the crystals were collected and washed with water (yield, 1.4 g.). The 2 : 3 : 4 : 6-tetramethoxyphenyl 4-methoxystyryl ketone was recrystallised from methyl alcohol (Found: C, 66.6; H, 6.0%). It then melted, alone or mixed with  $\beta$ -carthamidin pentamethyl ether, at  $112^{\circ}$  and agreed with this substance in all its properties. The absorption spectra of the two substances in  $N/5000$ -alcoholic solution, kindly photographed by Mr. Sakurai, the iron arc being used as a light source, were identical in every respect. Both showed a very wide band with its centre at about  $\lambda$  3300 Å. and another smaller band at about  $\lambda$  2700 Å. Indications of sharp narrow bands were observed in both cases in the region about  $\lambda$  3800 Å.

The author desires to thank the Keimeikai Society and the Department of Education for grants. She also wishes to express her appreciation of the helpful interest shown by Prof. Majima and the kind assistance of Miss Matsuguma.

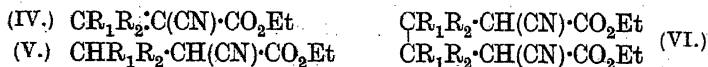
CIV.—*Syntheses of Cyclic Compounds. Part VI.*  
3- and 4-Methylcyclohexanones.

By ARTHUR ISRAEL VOGEL and MARIAM P. OOMMEN.

THE principal object of the present investigation was to determine the influence of the substitution of a methyl group for hydrogen in the 3- and 4-positions upon the character and the configuration of the *cyclohexane* ring. The only previous work on this subject appears to be that of Birch and Thorpe (J., 1922, **121**, 1821), who found that the bridged *spiro*-compounds (I), where  $R_1R_2C$  is 3-



and 4-methylcyclohexane, decomposed completely into the open-chain compound (III) on treatment with alkali under standard conditions, a result in contrast with that obtained with the unsubstituted *cyclohexane* ring ( $R_1R_2C = \text{cyclohexane}$ ), where the *spiro*-compound (II) was produced (Birch, Gough, and Kon, J., 1921, **119**, 1315). It is doubtful whether this method of comparing stabilities of ring systems, in its present state, is of any great value, since all the compounds (I) with substituents,  $R_1R_2C$ , other than *cyclohexane* are converted into the open-chain compounds (III) under the conditions employed and no means have yet been found for distinguishing between the rates of fission of individual members of the series. The method adopted in the present research is that described by one of us (Vogel, J., 1928, 2010) for the comparison of substituent groups and ring systems. The cyano-esters (IV)



were prepared by the condensation of the ketones with ethyl cyanoacetate in the presence of piperidine and reduced in ethereal solution with moist aluminium amalgam; the relative yields of the unimolecular (V) and the bimolecular products (VI) are shown in Table I,

TABLE I.

$CR_1R_2 \cdot C(CN) \cdot CO_2Et$	Yield % (V).	Yield % (VI).
$CR_1R_2 = \text{cyclopentane}$ .....	79	13
$= \text{cyclohexane}$ .....	84	6
$= 3\text{-methylcyclohexane}$ .....	83	6
$= 4\text{-methylcyclohexane}$ .....	87	4

the values for the *cyclopentane* and *cyclohexane* compounds being included for purposes of comparison: in so far as the yields of the

bimolecular compounds—which owing to their relatively slight volatility are employed for comparative purposes—are concerned, there seems to be no essential difference in behaviour between the unsubstituted and the methyl-substituted *cyclohexane* rings.

The unsaturated cyano-esters have the  $\alpha\beta$ -structure: the  $\beta\gamma$ -isomeride is present, if at all, in very small quantity. The  $\beta\gamma$ -structures assigned to the cyano-esters derived from 3- and 4-methyl-*cyclohexanones* by Harding, Haworth, and Perkin (J., 1908, 93, 1943) and by Harding and Haworth (J., 1910, 97, 486) require correction: the esters are completely reduced by moist aluminium amalgam and no definite evidence has been obtained of the presence of any appreciable quantity of unsaturated isomerides in the reduction products.

Prolonged hydrolysis of the reduced cyano-esters (V) with alcoholic potassium hydroxide afforded the corresponding malonic acids, the constitution and saturated character of which were proved by their synthesis from the iodides and ethyl sodiomalonate (compare Zelinski and Alexandrow, *Ber.*, 1901, 34, 3885).

Some physical properties of the pure ketones\* are recorded in Table II (compare Schoorl, *Rec. trav. chim.*, 1929, 48, 935). The

TABLE II.  
*cycloHexanones.*

	2-Methyl.	3-Methyl.	4-Methyl.
B. p. (mm.) .....	165°/757	169°/748	171°/747
$n_D^{20}$ .....	1.4484	1.4463	1.4455
$d_4^{20}$ .....	0.9261	0.9141	0.9151
$[R_L]_D$ (obs.) .....	32.45	32.69	32.61
$[R_L]_D$ (calc.) .....	32.34	32.34	32.34
$\gamma^{20}$ .....	31.99	31.23	31.04
$[P]$ (obs.) .....	288.2	290.0	289.6
$[P]$ (calc.) .....	288.1	288.1	288.1

refractive indices were measured at about 20°; the exact temperatures are given in the Experimental section. The surface tensions and the densities were determined over a range of temperatures and have been reduced to 20°, a linear variation with temperature being assumed. The parachors,  $[P]$  (obs.), were calculated by the usual formula. The parachors,  $[P_1]$ , for the corresponding cyclic hydrocarbons can be evaluated from the observed values for the cyclic ketones by substituting Sugden's values of 2H for :O. If, now, from these the parachor for the simple *cyclohexane* ring be found by replacing the value for CH<sub>3</sub> by that for H, the contribution per

\* The results for 2-methyl-*cyclohexanone* have been included for the sake of completeness.

$\text{CH}_2$  group,  $[P'_1/n]$ , which is an important criterion of the configuration of the ring (Vogel, J., 1928, 2018), can be calculated : the results (Table III, which includes the previous results for the

TABLE III.

	6-Ring.	2-Methyl.	3-Methyl.	4-Methyl.
$[P_1]$ .....	242.4	279.2	281.0	280.6
$[P'_1/n]$ .....	40.4	40.0	40.3	40.3

unsubstituted 6-ring) are in close agreement with that obtained from the observed parachor for the simple *cyclohexane* ring and thus provide further support for the view that there is no essential difference in configuration between the unsubstituted *cyclohexane* ring and that present in 3- and 4-methyl*cyclohexanones*.

## EXPERIMENTAL.

The 3- and 4-methyl*cyclohexanones* used were the pure products supplied by the Deutsche Hydrierwerke Aktiengesellschaft.

4-Methyl*cyclohexane* Series.

Ethyl 4-methyl*cyclohexylidene*-1-cyanoacetate was prepared by the condensation of 4-methyl*cyclohexanone* and ethyl cyanoacetate in the presence of piperidine (Harding, Haworth, and Perkin, *loc. cit.*) in ca. 60% yield. It had b. p.  $172^\circ/21$  mm. (Harding, Haworth, and Perkin give b. p.  $165$ – $168^\circ/14$  mm.),  $d_{40}^{21.2}$  1.0227,  $n_D^{21.2}$  1.4882,  $[R_L]_D$  58.38 (calc., 56.42).

*Ethyl* 4-methyl*cyclohexyl*-1-cyanoacetate (as V).—The preceding ester (100 g.) was reduced with 150 g. of moist aluminium amalgam in ether (Vogel, J., 1927, 594; 1928, 2010) : there was a period of induction of about 1.5 hours and the reaction was complete after 7 hours. The product was worked up in the usual manner and distilled, *ethyl* 4-methyl*cyclohexyl*-1-cyanoacetate (87 g.) passing over at  $160$ – $169^\circ/21$  mm. (more than 90% at  $163^\circ/21$  mm.). The viscid residue, having been washed several times with light petroleum (b. p.  $40$ – $60^\circ$ ), crystallised when left over-night in a vacuum over concentrated sulphuric acid (yield, 4 g.); it melted at  $75^\circ$  (softening at  $65^\circ$ ) and was the bimolecular *cyano-ester* (Found : *M*, in camphor, 421.  $\text{C}_{24}\text{H}_{36}\text{O}_4\text{N}_2$  requires *M*, 418). The liquid reduction product after redistillation had b. p.  $162^\circ/20$  mm.,  $d_{40}^{22.2}$  1.0018,  $n_D^{22.2}$  1.4585, whence  $[R_L]_D$  57.03 (calc., 56.89) (Found : C, 68.6; H, 9.1.  $\text{C}_{12}\text{H}_{19}\text{O}_2\text{N}$  requires C, 68.8; H, 9.2%).

4-Methyl*cyclohexyl*-1-malonic Acid.—Solutions of ethyl 4-methyl*cyclohexyl*-1-cyanoacetate (30 g.) in rectified spirit (160 g.) and of potassium hydroxide (100 g.) in water (100 g.) were mixed, heated on the steam-bath for 24 hours (the evolution of ammonia had then



ceased), and evaporated to dryness. The residue was triturated several times with ether to remove any unchanged ester and acidified with dilute sulphuric acid; 4-methylcyclohexyl-1-malonic acid, m. p.  $172^{\circ}$ , precipitated in almost quantitative yield, had m. p.  $182$ — $183^{\circ}$  after several crystallisations from formic acid (*d* 1.2) (Hope and Perkin, J., 1909, 95, 1367, give m. p.  $177$ — $178^{\circ}$ ) (Found: equiv., by titration with baryta, 101. Calc., 100). An additional small quantity was extracted by ether from the filtrate after saturation with ammonium sulphate.

*Synthesis of 4-Methylcyclohexyl-1-malonic Acid from 4-Methylcyclohexyl Iodide and Ethyl Sodiomalonnate.*—4-Methylcyclohexanone was reduced with sodium and moist ether (compare Bentley, J., 1895, 67, 264) to the alcohol, b. p.  $174^{\circ}/760$  mm. This (116 g.) was treated with red phosphorus (9.5 g.) and iodine (90 g.), rise of temperature being prevented, and after 12 hours the whole was heated on the steam-bath for 2 hours, and 4-methylcyclohexyl iodide isolated in the usual manner (compare Bentley, *loc. cit.*). It had b. p.  $63^{\circ}/3.5$  mm.,  $d_{4}^{20.9^{\circ}}$  1.5086,  $n_D^{20.9^{\circ}}$  1.5325, whence  $[R_L]_D$  46.04 (calc., 45.13) (Found: I, 56.6.  $C_7H_{13}I$  requires I, 56.7%). When freshly distilled, the iodide is a colourless mobile liquid with a characteristic odour.

The reaction between 4-methylcyclohexyl iodide (127 g.; 1 mol.) and ethyl sodiomalonate (2 mols.: \* compare Zelinski and Alexandrow, *loc. cit.*; prepared from 90.7 g. of ethyl malonate, 13.05 g. of sodium, and 200 c.c. of dry alcohol) was carried out in the way described by Hope and Perkin (J., 1909, 95, 1363). The product on distillation gave first ethyl malonate and 4-methylcyclohexyl iodide; ethyl 4-methylcyclohexyl-1-malonate then passed over at  $164$ — $168^{\circ}/29$  mm. On redistillation, it boiled at  $161$ — $163^{\circ}/18$  mm. (Hope and Perkin give b. p.  $163$ — $165^{\circ}/20$  mm.); yield, 75 g. or 55%.

The acid obtained by the hydrolysis of the ester with alcoholic potassium hydroxide on the steam-bath melted, after three crystallisations from formic acid, at  $182$ — $183^{\circ}$  (decomp.) (Found: equiv., by titration, 100.5) and was identical (mixed m. p.) with 4-methylcyclohexyl-1-malonic acid prepared as described above. From the filtrate from the precipitated acid, saturated with ammonium sulphate, ether extracted about 2 g. of an acid, m. p.  $100$ — $110^{\circ}$ , and  $110^{\circ}$  after recrystallisation from benzene: this was probably impure *r*-3-methylcyclohexyl-1-malonic acid (m. p.  $120$ — $121^{\circ}$ ; mixed m. p.  $116$ — $117^{\circ}$ ) (Found: equiv., 101), but the quantity was too small for identification.

\* A slightly smaller yield was obtained with equimolecular quantities.

### 3-Methylcyclohexane Series.

Ethyl 3-methylcyclohexylidene-1-cyanoacetate was prepared in *ca.* 60% yield by the condensation of the ketone with ethyl cyanoacetate in the presence of piperidine (Harding and Haworth, *loc. cit.*) and had b. p. 160—163°/15 mm. A middle fraction prepared for analysis had b. p. 163°/16 mm.,  $d_4^{20}$  1.0288,  $n_D^{20}$  1.4914, whence  $[R_L]_D$  58.36 (calc., 56.42) (Found: C, 69.2; H, 8.2. Calc.: C, 69.5; H, 8.3%).

*Ethyl r-3-Methylcyclohexyl-1-cyanoacetate.*—The preceding ester (100 g.) was reduced with 150 g. of moist aluminium amalgam in ether (7 hours). The product gave on distillation *ethyl r-3-methylcyclohexyl-1-cyanoacetate* (83 g.), which passed over at 150—153°/15 mm., mainly at 152°/15 mm. The residue crystallised after being treated with light petroleum (b. p. 40—60°) in the manner detailed for the 4-methyl compound; yield, 6 g. It had m. p. 76° (softening at 65°) and was probably a mixture of isomeric bimolecular cyano-esters (Found: *M*, in camphor, 416.  $C_{24}H_{36}O_4N_2$  requires *M*, 418). The liquid reduction product after redistillation had b. p. 152°/15 mm.,  $d_4^{20}$  1.0022,  $n_D^{20}$  1.4586, whence  $[R_L]_D$  57.02 (calc., 56.89) (Found: C, 68.4; H, 9.1.  $C_{12}H_{19}O_2N$  requires C, 68.8; H, 9.2%).

*r-3-Methylcyclohexyl-1-malonic Acid.*—The hydrolysis of ethyl 3-methylcyclohexyl-1-cyanoacetate was effected (36 hours) as described under the 4-methyl compound. The resultant oily acid, crystallised twice from benzene, formed needles, m. p. 115—116° (rapidly heated), 120—121° (slowly heated) (Found: C, 60.3; H, 8.1; equiv., 99.  $C_{10}H_{16}O_4$  requires C, 60.0; H, 8.1%; equiv., 100). *r-3-Methylcyclohexyl-1-malonic acid* is soluble in water, chloroform, ether, and formic acid; it is sparingly soluble in dilute hydrochloric acid and in benzene when cold but dissolves readily on warming (the corresponding 4-methyl compound is very soluble in ether, but dissolves readily in water, chloroform, and formic acid only when warm). The presence of an isomeric acid could not be detected.

*Synthesis of r-3-Methylcyclohexyl-1-malonic Acid from 3-Methylcyclohexyl Iodide and Ethyl Sodiomalonate.*—In the ways already indicated, 3-methylcyclohexanone was converted through the alcohol, b. p. 174°/760 mm., into 3-methylcyclohexyl iodide,\* b. p. 61—63°/3 mm. (Knoevenagel, *Annalen*, 1897, 297, 154, gives b. p. 82—83°/10 mm.) (yield, almost quantitative), a colourless mobile liquid with a characteristic odour when freshly distilled.

The condensation with ethyl sodiomalonate was carried out, in

\* This probably contained some of the 4-methyl iodide (see p. 773).

the manner already described, with 97 g. of the iodide, 10 g. of sodium, 200 c.c. of dry alcohol, and 138 g. of ethyl malonate. The product, b. p. 159—163°/19 mm. (45 g.), hydrolysed with twice the calculated quantity of alcoholic potassium hydroxide, gave an almost quantitative yield of oily acids, which solidified on trituration with benzene. The acids were treated with cold formic acid: the insoluble portion, recrystallised three times from hot formic acid, melted at 182—183° and its identity with 4-methylcyclohexyl-1-malonic acid was confirmed by direct comparison and by a mixed m. p. determination (Found: equiv., 99); the soluble portion was evaporated to dryness on the steam-bath, the resultant oil triturated with a small quantity of benzene, and the solid thus obtained treated with cold formic acid. The residue obtained on evaporation of the filtrate melted at 110—111° after several crystallisations from benzene (Found: C, 60.1; H, 8.1%; equiv., 99.5). This acid resembles *r*-3-methylcyclohexyl-1-malonic acid, prepared from the cyano-ester, very closely in properties (solubility, crystalline form, etc.) and is probably identical with it; a mixture of the two melted at 117—118°. There appeared to be a very small quantity of an isomeric acid present which could not be removed by fractional crystallisation from common organic solvents.

In order to put the surprising nature of the above result, *viz.*, the formation of approximately equal quantities of 3- and 4-methylcyclohexylmalonic acids in the condensation of 3-methylcyclohexyl iodide and ethyl sodiomalonate, beyond all question, the whole experiment was repeated with pure 3-methylcyclohexanone prepared from the semicarbazone, m. p. 189—190°. (The ketone employed for the above experiments gave a quantitative yield of a semicarbazone, m. p. 186°, and 189—190° after two crystallisations from dilute methyl alcohol.) The pure ketone was successively converted into the alcohol, b. p. 173°/760 mm., the iodide, b. p. 61—62°/3 mm., and ethyl methylcyclohexylmalonate, b. p. 158—162°/22 mm., mainly 160°/22 mm. (47 g. of the iodide furnished 23 g. of the malonic ester). The ester on hydrolysis gave the same mixture of acids as before. This remarkable reaction will be more fully investigated: possibly, during the conversion of 3-methylcyclohexanol into the iodide and under the influence of the phosphorus iodides present, dehydration occurs, followed by addition of hydrogen iodide in the two positions leading to the formation of 3- and 4-methylcyclohexyl iodides.

*Determination of Surface Tensions and of Densities over a Range of Temperatures. Calculation of the Parachor.*

The apparatus and procedure employed in these determinations were those already described (Vogel, J., 1928, 2027). The correction

for the meniscus was 0.24 mm., and the mean constant  $K$  1.8746. The symbols in the tables have already been defined (Vogel, *loc. cit.*).

All the ketones were regenerated, by means of oxalic acid, from the semicarbazones, which had been recrystallised from rectified spirit until the m. p.'s were constant.

2-Methylcyclohexanone,  $M = 112.10$ , b. p.  $165^\circ/757$  mm.,  $n_D^{19.4^\circ}$  1.4484,  $d_4^{19.4^\circ}$  0.9255, whence  $[R_L]_D$  32.45 (calc., 32.34). Semicarbazone, m. p.  $195-196^\circ$ .

Densities determined:  $d_4^{18.9^\circ}$  0.9270;  $d_4^{61.4^\circ}$  0.8927;  $d_4^{81.4^\circ}$  0.8756.

$t.$	$h.$	$H.$	$d_4^{t^\circ}$	$\gamma.$	Parachor.
22.3°	18.55	18.31	0.9253	31.76	287.6
61.4	16.84	16.60	0.8927	27.78	288.3
81.6	16.04	15.80	0.8770	25.98	288.6
					Mean 288.2

3-Methylcyclohexanone,  $M = 112.10$ , b. p.  $169^\circ/747.5$  mm.,  $d_4^{18.7^\circ}$  0.9151,  $n_D^{18.7^\circ}$  1.4463, whence  $[R_L]_D$  32.69. Semicarbazone (also recrystallised twice from methyl alcohol), m. p.  $191^\circ$ .

Densities determined:  $d_4^{18.2^\circ}$  0.9155;  $d_4^{61.6^\circ}$  0.8816;  $d_4^{83.1^\circ}$  0.8636.

$t.$	$h.$	$H.$	$d_4^{t^\circ}$	$\gamma.$	Parachor.
21.5°	18.40	18.16	0.9129	31.08	289.9
63.1	16.62	16.38	0.8806	27.04	290.3
83.5	15.62	15.38	0.8648	24.93	289.7
					Mean 290.0

4-Methylcyclohexanone,  $M = 112.10$ , b. p.  $171^\circ/747$  mm.,  $d_4^{19.3^\circ}$  0.9159,  $n_D^{19.3^\circ}$  1.4455, whence  $[R_L]_D$  32.61. Semicarbazone, m. p.  $197^\circ$ .

Densities determined:  $d_4^{18.2^\circ}$  0.9164;  $d_4^{62.6^\circ}$  0.8831;  $d_4^{84.3^\circ}$  0.8648.

$t.$	$h.$	$H.$	$d_4^{t^\circ}$	$\gamma.$	Parachor.
20.2°	18.33	18.09	0.9148	31.02	289.2
62.6	16.62	16.38	0.8831	27.05	289.6
84.3	15.76	15.52	0.8658	25.19	290.0
					Mean 289.6

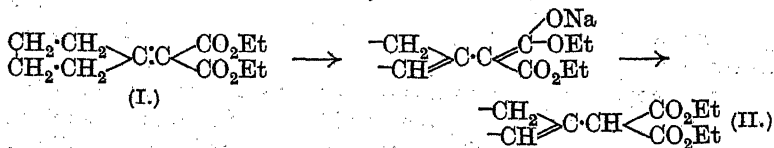
In conclusion, the authors wish to express their thanks to Professor J. F. Thorpe, F.R.S., and to Dr. M. A. Whiteley for their kind interest in this investigation, and to the Chemical Society for a grant which has helped to defray its cost.

CV.—*The Chemistry of the Three-carbon System.*  
 Part XXIV. *The Regeneration of Esters from*  
*their Sodio-derivatives.*

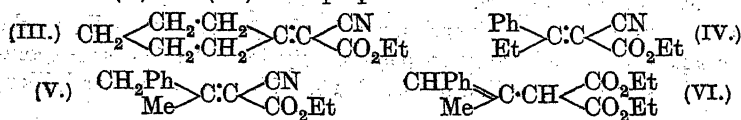
By WILFRED EYNON HUGH and GEORGE ARMAND ROBERT KON.

It has already been suggested that the function of activating groups in enhancing the mobility of a three-carbon system is connected with the capacity of the mobile hydrogen to enter such groups (compare Kon and Speight, J., 1926, 2727). For instance, the rapid interconversion of  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated ketones in presence of sodium ethoxide is no doubt due to the formation of the sodio-derivatives of the enolic form of the ketone; or, in terms of the ionic hypothesis of tautomerism, the change proceeds through the establishment of an equilibrium between the ions of the two keto-forms and the common enol ion (Ingold, Shoppee, and Thorpe, J., 1926, 2477; Linstead, J., 1929, 2498). There are thus two equilibria—one involving only the keto-enol system of the activating group, the other the three-carbon system as well.

One of the chief differences between keto-enol and three-carbon systems is the greater mobility of the former; it should, therefore, be possible to realise conditions under which only the keto-enol change can proceed to completion, without causing mobility of the adjacent three-carbon system and thus giving rise to a "false equilibrium." This would be expected in systems sufficiently acidic to form stable enols and in the absence of polar catalysts. For instance, if the  $\alpha\beta$ -unsaturated ethyl *cyclopentylidenemalonate* (I) were converted into the sodio-derivative, which is necessarily derived from the  $\beta\gamma$ -form, and hydrogen could be introduced in place of sodium under conditions precluding complete equilibration, the enol produced should be converted into its own keto-form, which is the hitherto unknown  $\beta\gamma$ -isomeride (II).



The ester (I) and ethyl  $\alpha$ -cyanocyclohexylideneacetate (III) were chosen for the investigation; in addition, ethyl  $\alpha$ -cyano- $\beta$ -ethylcinnamate (IV) and ethyl  $\alpha$ -cyano- and  $\alpha$ -carbethoxy- $\gamma$ -phenyl- $\beta$ -methylbutenoates (V) and (VI) were prepared:



Although the results so far obtained are of a preliminary character, they show that it is possible to arrest three-carbon tautomerism to some extent whilst allowing keto-enol equilibrium to be established in the manner suggested. The method adopted consists in forming the sodio-derivative of the ester, preferably in a neutral solvent, and decomposing it by the addition of a weak organic acid such as benzoic acid, at a low temperature; after removal of the sodium benzoate, the ester is isolated by evaporation of the solvent, somewhat on the lines of Knorr's classical work on ethyl acetoacetate.

Negative results were always obtained with the cyano-ester (III), but the ester (I) gave definite indications of a change. The ester obtained from the sodio-derivative not only had a lower boiling point, density, and refractive index, but showed a considerable increase in additive power towards iodine chloride: all these properties are consistent with the  $\beta\gamma$ -unsaturated structure. Oxidation with ozone led to a substance having the properties both of an aldehyde and of a  $\beta$ -ketonic ester, as would be expected from such a structure.

Even careful hydrolysis of the new ester gave the original acid and no isomeride has yet been obtained.

Although esterification of the pure acid by way of its silver salt (Kon and Speight, *loc. cit.*) leads to the pure  $\alpha\beta$ -ester (I), esterification in presence of a strong mineral acid gives an ester containing a considerable quantity of the  $\beta\gamma$ -form, in some cases as much as is present in the ester prepared by regeneration from the sodio-derivative. The esters obtained by different processes differ considerably in properties; that obtained by the direct condensation of cyclopentanone with ethyl malonate is mainly the  $\alpha\beta$ -ester, whereas acidification of the sodio-derivative in alcoholic solution without special precautions yields an ester containing a considerable proportion of the  $\beta\gamma$ -form: this "equilibrium ester" appears to have a fairly constant composition; it is difficult to estimate the proportion of the two isomerides in it by the iodometric method, as the pure  $\beta\gamma$ -ester has in all probability not been obtained.

It was hoped to gain a means of comparison by determining the iodine addition of the pure  $\beta\gamma$ -ester of the cyclohexane series (ethyl cyclohexenylmalonate). This ester was prepared by the silver-salt process from the pure acid, which had a very high affinity for iodine (91.4%), in contrast with that of the cyclopentane acid (0.35%); but the ester had a low iodine value and therefore was valueless for our purpose.

Cyano-esters with a phenyl group in the  $\beta$ - and especially in the  $\gamma$ -position appeared likely to pass readily into the  $\beta\gamma$ -forms (compare Linstead and Williams, J., 1926, 2735; Johnson and Kon,

*ibid.*, p. 2748), and for this reason the esters (IV) and (V) were synthesised: they were found to have the  $\alpha\beta$ -unsaturated structure, unlike Linstead and Williams's cyano-ester, but although they yielded  $\beta\gamma$ -unsaturated alkylation products, the  $\beta\gamma$ -isomerides could not be obtained from them. The condensation product of benzyl methyl ketone and ethyl malonate was abnormal in structure, and the acid obtained from it on hydrolysis had lost the elements of water (compare Linstead and Williams, *loc. cit.*); in addition, the double bond was already in the  $\beta\gamma$ -position, because the acid yielded benzaldehyde on oxidation: it has not yet been fully investigated.

#### EXPERIMENTAL.

*Ethyl  $\alpha$ -Cyanocyclohexylideneacetate* (III).—The ester was prepared by the method of Harding, Haworth, and Perkin (J., 1908, 93, 1949) and had the properties recorded by Birch, Kon, and Norris (J., 1923, 123, 1361): the value 53.94 given there for  $[R_L]_D$  is a misprint for 53.594.

The  $\alpha\beta$ -structure of the ester was confirmed by oxidation: 5 g. of the ester were treated with the required amount of ice-cold neutral 3% aqueous potassium permanganate and the solution was kept for an hour; cyclohexanone, isolated by steam-distillation and extraction with ether, was identified in the form of semicarbazone (m. p. and mixed m. p. 165–166°).

The ester (1/10 g.-mol.) was slowly added to 2.3 g. of "molecular" sodium covered with dry ether. The reaction was vigorous, but it was difficult to induce all the sodium to react. Finally, light petroleum was added and the precipitated sodio-derivative was collected rapidly, suspended in dry ether, and treated with 1/10 mol. of benzoic acid in dry ether. When the yellow colour had disappeared, the ethereal solution was washed with aqueous sodium carbonate and with water, dried over calcium chloride, and evaporated, finally in a vacuum. The properties of the ester obtained,  $d_4^{16.5}$  1.0616,  $n_D^{18.5}$  1.48327, changed but little after distillation (b. p. 160–164°/18 mm.). In another experiment the preparation of the sodio-derivative was carried out in benzene solution, which was preferable to ether, with a similar result. In a third experiment the regeneration was carried out at  $-20^\circ$  by means of dry hydrogen chloride or by means of less than the calculated amount of glacial acetic acid (containing a little acetic anhydride to ensure the absence of water) and the washing was omitted. In all cases the ester had the same iodine addition (about 5% in one hour) as that of the pure  $\alpha\beta$ -ester, and this did not change on treatment with sodium ethoxide. The change in physical properties was therefore clearly due to a certain amount of reduction of the cyano-ester during the formation

of the sodio-derivative. In order to obviate this, sodium ethoxide, freed from excess of alcohol, was used to form the sodio-derivative, which was then precipitated with a large volume of light petroleum and treated with benzoic acid; no indication of the existence of a  $\beta\gamma$ -ester was obtained.

*Ethyl cyclopentylidenemalonate* (I).—The ester was prepared by the method of Kon and Speight (*loc. cit.*), but it was found convenient to modify the process of isolation as follows. The almost black reaction product of cyclopentanone and ethyl malonate was mixed with 3–4 volumes of light petroleum and well shaken; the acetanilide and the tarry matter formed were precipitated and the very troublesome and wasteful process of washing was thus obviated. The almost clear petroleum solution was filtered, washed with water and alkali, and dried; on evaporation it gave a fair yield of the required ester,  $d_4^{23.5}$  1.0613,  $n_D^{23.5}$  1.4696, iodine addition in 1 hour (in chloroform solution by the method of Linstead and May; J., 1927, 2565) 11.1%.

The ester on hydrolysis gave the acid already described by Kon and Speight; the iodine addition of the pure acid in sodium bicarbonate solution was only 0.35% in 1 hour. This was esterified through the silver salt and the ester produced had b. p.  $160^\circ/20$  mm.,  $d_4^{23.0}$  1.0618,  $n_D^{23.0}$  1.47301,  $[R_L]_D$  59.75 (compare Kon and Speight, *loc. cit.*), iodine addition in 1 hour 1.5%.

The first experiments on the regeneration of the ester from its sodio-derivative were carried out with "molecular" sodium in benzene in the manner described on p. 777; a definite indication of change was obtained. In later experiments, sodium ethoxide was prepared from specially dehydrated alcohol, the excess of alcohol carefully removed in a vacuum at  $100^\circ$ , and the ester added together with some petroleum (b. p.  $40$ – $60^\circ$ ); when the sodio-derivatives had formed, more petroleum was added and the solid allowed to settle. The petroleum solution was decanted, the residue again washed with petroleum (the sodio-derivative can also be filtered off), and benzoic acid in dry ether added to the sodio-derivative with shaking, more petroleum then being added. The gelatinous sodium benzoate was filtered off, and the petroleum solution washed with dilute aqueous sodium carbonate, washed, dried, and evaporated. The ester, obtained in 30–50% yield, varied but little in properties; the best specimen had b. p.  $147$ – $148^\circ/19$  mm.,  $d_4^{24.5}$  1.0511,  $n_D^{24.5}$  1.45743,  $[R_L]_D$  58.37 (calc., 58.02), and an iodine addition of 38.4%; it consisted, therefore, mainly of *ethyl  $\Delta^1$ -cyclopentenylmalonate* (II) (Found: C, 64.0; H, 8.0.  $C_{12}H_{18}O_4$  requires C, 63.7; H, 8.0%). The molecular refraction shows an exaltation of only 0.35 unit (comparable with that found by Kon and Speight



for the  $\alpha$ -methyl derivative and for cyclohexenylmalonic ester), due, no doubt, to the conjugation of the two carbethoxy-groups. The ester did not give a colour with ferric chloride.

The petroleum solution decanted from the sodio-derivative was acidified with hydrochloric acid, washed with sodium carbonate solution, and evaporated, yielding a further quantity of ester; this had a lower iodine addition—about 30%—and presumably was the "equilibrium ester."

A specimen of the  $\beta\gamma$ -ester, prepared by direct esterification as described below, was treated with alcoholic sodium ethoxide, and the product isolated without special precautions; it had b. p. 142—150°/20 mm.,  $d_4^{20}$  1.0551,  $n_D^{20}$  1.46191,  $[R_L]_D$  58.91, and an iodine addition of 28.0%, and was thus very similar to the preceding ester.

When sodium methoxide was used in place of the ethoxide in the above preparation, the product obtained was *methyl ethyl cyclopentenylmalonate*; after redistillation it boiled at 137—138°/18 mm. and had  $d_4^{20}$  1.09776,  $n_D^{20}$  1.46380, iodine addition about 37% (Found: C, 62.0; H, 7.3.  $C_{11}H_{16}O_4$  requires C, 62.2; H, 7.6%).

The  $\beta\gamma$ -ester was also produced when the solid  $\alpha\beta$ -acid was kept in contact with 1% alcoholic hydrogen chloride (8 vols.) at room temperature; the acid slowly dissolved in the course of 10 days and the ester was then isolated and the considerable unesterified portion again treated with alcoholic hydrogen chloride. The ester had b. p. 146—148°/20 mm.,  $d_4^{20}$  1.0546,  $n_D^{20}$  1.45923,  $[R_L]_D$  58.65; the iodine addition was 37.5%, so the ester was evidently mainly the  $\beta\gamma$ -form. In another instance, the acid was boiled with a saturated solution of hydrogen chloride in absolute alcohol for a short time; the ester produced was mainly the  $\alpha\beta$ -form.

The  $\beta\gamma$ -ester, dissolved in ethyl acetate, was treated with ozonised oxygen at 0°, the ozonide was freed from the solvent and decomposed by warm water, and the product isolated by means of ether and distilled. Much decomposition (elimination of alcohol?) took place and a definite fraction was not obtained, the greater part boiling between 140° and 150°/11 mm. This gave an intense blue colour, slowly changing to red, with ferric chloride, and Schiff's test, and was thus an aldehyde and a  $\beta$ -ketonic ester, presumably  $CHO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH(CO_2Et)_2$ ; the carbon content, however, agrees better with the formula  $CHO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot CH_2 \cdot CO_2Et$  (Found: C, 59.1; H, 7.2.  $C_{12}H_{18}O_6$  requires C, 55.8; H, 7.0%.  $C_9H_{14}O_4$  requires C, 58.0; H, 7.6%); crystalline derivatives could not be obtained from it.

The  $\beta\gamma$ -ester was hydrolysed by means of cold 5% alcoholic sodium hydroxide, and the acid isolated in the usual manner. The

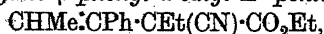
$\alpha\beta$ -acid, m. p.  $171^\circ$ , was isolated in quantity; a more soluble constituent was also present, but it could not be obtained pure. An attempt to prepare the pure  $\beta\gamma$ -ester by partial esterification of the crude acid obtained above (compare Eccott and Linstead, J., 1929, 2153) was unsuccessful; the ester produced had a slightly lower iodine addition than the specimen from which it was derived.

*Ethyl cycloHexenylmalonate*.—The pure acid, m. p.  $150^\circ$  (Kon and Speight), was found to have an iodine addition of 91.4% in 1 hour. It was esterified through the silver salt, giving an ester, b. p.  $160^\circ/20$  mm.,  $d_4^{20.9^\circ}$  1.0504,  $n_D^{20.9^\circ}$  1.4646, iodine addition 7.5%. Another specimen of the ester was separated into two portions by distillation, but both had practically identical properties and iodine additions (7.4 and 8.1%). After treatment of the ester with sodium ethoxide without special precautions, the iodine addition rose somewhat (9.6%). The ozonisation of the ester was repeated, Kon and Speight's results being confirmed.

*Ethyl  $\alpha$ -Cyano- $\beta$ -ethylcinnamate* (IV).—Ethyl cyanoacetate (57 g.) and propiophenone (67 g.) were mixed with 1 c.c. of piperidine and heated on the steam-bath for 3 days. The product was dissolved in ether, washed with dilute hydrochloric acid and with water, dried, and distilled. Most of the initial material was recovered, but some 12 g. of an oil, b. p.  $182$ — $188^\circ/17$  mm., were collected. The yield of this oil could be increased to about 28 g. by adding anhydrous sodium sulphate to the reaction mixture to facilitate the separation of the water formed in the reaction. Condensation also took place in the presence of sodium ethoxide in alcohol (11.5 g. of sodium in 150 c.c. of alcohol), the mixture being heated until the whole of the solid ethyl sodiocyanoacetate had disappeared (about 2 hours); the yield of high fraction contained in the neutral reaction product was about 20 g. The recovered material could be used again. The fraction of b. p.  $182$ — $188^\circ/17$  mm. gave on careful redistillation a large fraction, b. p.  $185^\circ/15$  mm., consisting of *ethyl  $\alpha$ -cyano- $\beta$ -ethylcinnamate*,  $d_4^{19.3^\circ}$  1.0695,  $n_D^{19.3^\circ}$  1.53803,  $[R_L]_D$  67.01 (calc., 64.26) (Found: C, 73.2; H, 6.5.  $C_{14}H_{15}O_2N$  requires C, 73.4; H, 6.6%). The structure of the ester was confirmed by oxidation with permanganate exactly as described on p. 777; propiophenone was obtained in good yield and identified in the form of its semicarbazone.

All attempts to obtain the  $\beta\gamma$ -isomeride from the sodio-derivative were unsuccessful.

The ester was readily ethylated through its sodio-derivative, prepared with the aid of "molecular" sodium in benzene. The new ester, *ethyl  $\alpha$ -cyano- $\beta$ -phenyl- $\alpha$ -ethyl- $\Delta^8$ -penteenoate*,



had b. p. 182—186°/16 mm.,  $d_4^{17.2}$  1.0545,  $n_D^{17.2}$  1.52175,  $[R_L]_D$  74.33 (calc., 73.50) (Found: C, 74.9; H, 7.3.  $C_{16}H_{19}O_2N$  requires C, 74.7; H, 7.4%). Like other similar compounds, the ethylated cyano-ester readily lost carbethoxyl in the form of ethyl carbonate on being kept with an equivalent of sodium ethoxide at 35° for 24 hours, giving  $\beta$ -phenyl- $\alpha$ -ethyl- $\Delta^a$ -pentenonitrile, b. p. 142—146°/14 mm.,  $d_4^{19.0}$  0.9856,  $n_D^{19.0}$  1.54052,  $[R_L]_D$  58.97 (calc., 57.98) (Found: C, 83.6; H, 7.7.  $C_{13}H_{15}N$  requires C, 84.3; H, 8.2%).

*Attempted Condensation of Propiophenone and Ethyl Malonate.*—It was not found possible to obtain a condensation product from these substances under any of the conditions tried.

*Ethyl  $\alpha$ -Cyano- $\gamma$ -phenyl- $\beta$ -methyl- $\Delta^a$ -butenoate (V).*—Benzyl methyl ketone (134 g.), ethyl cyanoacetate (113 g.), and piperidine (2.5 c.c.) were kept at room temperature for 3 days with occasional shaking. Water began to separate after about 3 hours. The mixture was worked up as described on p. 780, and the product distilled under reduced pressure; after unchanged materials had passed over, an oil was obtained which on redistillation gave 46 g. of the ester (V): a small quantity was also obtained from the lower fractions, and there was hardly any high-boiling fraction. The ester had b. p. 182—184°/11 mm.,  $d_4^{18.9}$  1.0790,  $n_D^{18.9}$  1.53401,  $[R_L]_D$  66.00 (calc., 64.26) (Found: C, 73.5; H, 6.6.  $C_{14}H_{15}O_2N$  requires C, 73.4; H, 6.6%). It gave benzyl methyl ketone in good yield (semi-carbazone, m. p. 189—190°) on oxidation with neutral permanganate, its structure thus being confirmed.

Attempts to obtain the  $\beta\gamma$ -isomeride were unsuccessful. From the sodio-derivative prepared with the aid of sodium ethoxide by the method described on p. 778, the ester was regenerated unchanged, the iodine addition being the same before and after the experiment (3.8% in 1 hour). When "molecular" sodium was used, some change in the physical properties of the ester took place, but this was due to reduction; no rise in iodine addition was observed.

The ester was ethylated as described on p. 780. The product did not boil uniformly, doubtless owing to the presence of a small amount of reduced material, but a considerable fraction, b. p. 190—192°/13 mm., was obtained consisting of ethyl  $\alpha$ -cyano- $\gamma$ -phenyl- $\beta$ -methyl- $\alpha$ -ethyl- $\Delta^b$ -butenoate,  $d_4^{18.2}$  1.0452,  $n_D^{18.2}$  1.51986,  $[R_L]_D$  74.76 (calc., 74.50) (Found: C, 74.4; H, 7.4.  $C_{16}H_{19}O_2N$  requires C, 74.7; H, 7.4%). When this ester was treated with sodium ethoxide, ethyl carbonate and  $\gamma$ -phenyl- $\beta$ -methyl- $\alpha$ -ethyl- $\Delta^a$ -butenonitrile,  $CH_2Ph \cdot CMe \cdot CEt \cdot CN$ , were produced. The latter on redistillation boiled at 159—161°/16 mm. and had  $d_4^{18.4}$  0.97806,  $n_D^{18.4}$  1.52469,  $[R_L]_D$  57.97 (calc., 57.98) (Found: C, 83.9; H, 8.3.  $C_{13}H_{15}N$  requires C, 84.3; H, 8.2%).

*Condensation of Benzyl Methyl Ketone with Ethyl Malonate.*—The condensation was carried out by the method of Kon and Speight (*loc. cit.*). From 1 g.-mol. of the ketone, about 10 g. of a fraction, b. p. 180—188°/14 mm., presumably consisting of the ester (VI), were obtained. On hydrolysis with alkali, the ester gave an acid,  $C_{12}H_{10}O_3$  (Found: C, 71.4; H, 5.1. *M*, by titration, 196.5.  $C_{12}H_{10}O_3$  requires C, 71.3; H, 5.0%; *M*, 202.  $C_{12}H_{12}O_4$  requires C, 65.5; H, 5.4%). On oxidation with alkaline permanganate the acid yielded benzaldehyde, which was identified by means of its semicarbazone.

The authors' thanks are due to the Royal Society for grants which have defrayed the cost of this investigation.

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## CVI.—*The Properties of the Chlorides of Sulphur.* *Part III. Dielectric Constants.*

By THOMAS MARTIN LOWRY and GILBERT JESSOP.

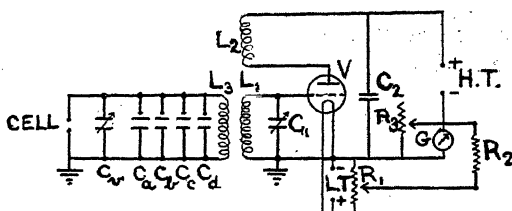
IN the two preceding papers of this series (J., 1927, 746; 1929, 1421), it has been shown (i) that sulphur dichloride,  $SCl_2$ , crystallises as a stable phase from a liquid chloride of sulphur containing from 59 to 65 atoms % of chlorine, and a new chloride,  $S_3Cl_4$ , separates in the range 57—59 atoms %; (ii) that sulphur dichloride in the liquid state is dissociated at atmospheric temperatures to the extent of about 16% according to the equation  $2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$ ; (iii) that sulphur tetrachloride,  $SCl_4$ , which is the stable solid phase over a wide range of compositions above 65 atoms % of chlorine, cannot be detected in the liquid phase; and (iv) that a liquid chloride of sulphur therefore behaves as a ternary mixture of mono- and di-chlorides and chlorine only. In the present paper these results have been confirmed by measurements of the dielectric constants of a series of samples ranging from sulphur monochloride to pure chlorine, which show that sulphur tetrachloride is stable in the solid phase, but cannot be detected in the liquid phase.

### EXPERIMENTAL.

*Methods.*—The apparatus used for the measurement of dielectric constants (compare Sayce and Briscoe, J., 1925, 127, 315) is shown in Fig. 1. It employs a valve generating circuit, but does not appear to be open to the objections which have been raised by many authors to such circuits. The stress applied to the dielectric must

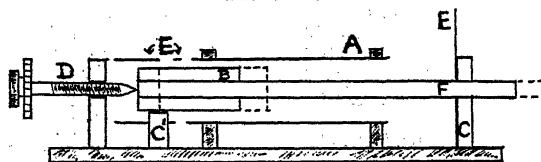
be small and of sine-wave form, without the harmonics of considerable amplitude which are found in most valve-operated circuits; and the apparent value of the capacity must not vary when the liquid shows a small conductivity. In the present apparatus these conditions are fulfilled in view of the fact that the circuit which contains the dielectric is not coupled directly to the valve;

FIG. 1.

*Apparatus for measuring dielectric constants.*

and experimental tests have shown that the introduction of a high resistance in parallel with the condenser merely reduces the accuracy of the measurement, without altering the absolute value of the constant. The main difficulties were (i) to construct a condenser of large capacity (150 cm.) which could be adjusted with great accuracy (within 0.01 cm.), and (ii) to construct a cell, which would hold only a small volume (5–10 c.c.) of a corrosive liquid, but could with-

FIG. 2.

*Variable condenser.*

stand an internal pressure of 1–2 atm., and be used at any temperature from  $-100^{\circ}$  to  $25^{\circ}$ .

(a) *Condensers.* The condenser of variable capacity and wide range included four fixed condensers,  $C_a$  to  $C_d$ , having capacities of about 10, 20, 40, and 80 cm. respectively, and a variable condenser,  $C_b$ , with a capacity of about 15 cm. The fixed condensers were made from air-spaced aluminium plates mounted on ebonite. One set of plates was connected to the earthed lining of the box containing the apparatus, and the other to small mercury cups which could be connected to the "live" side of the circuit by means of wire bridges operated from the outside of this box. The variable condenser,  $C_b$ , was cylindrical, as shown in Fig. 2, whereas Sayce and

Briscoe used a rotating-plate condenser. The "live" side was a fixed brass tube, A, mounted on ebonite blocks. The earthed plate was formed by an accurately turned brass cylinder, B, attached to a rod F, and was mounted on two rigid bearings, C and C', the latter, carrying the tube B, being V-shaped. The air gap between A and B was about 1 mm. The capacity of the condenser was varied with the help of a fine screw, D, against the point of which the end of the inner cylinder was pressed by a spring, which is not shown in the diagram. "End effects" were prevented by means of earthed guards, E. The condenser, which was used over a small range only,

FIG. 3.

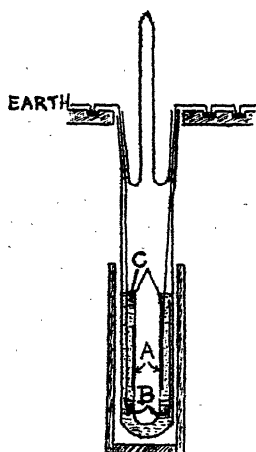
*Dielectric-constant cell.*

FIG. 4.

*Conductivity cell.*

as shown by the dotted lines, was calibrated against a small fixed condenser, and it was found that the variation of capacity was proportional to the rotation of the divided head of the screw D over the entire working range.

(b) *Cell.* The type generally used is shown in Fig. 3. The inner plate of the condenser consisted of a cylinder, A, of platinum foil, which was kept in shape by being mounted on a short closed glass tube. Surrounding this, and separated from it by a gap of about 1 mm., was a stout platinum cylinder, B, which formed the outer plate of the condenser. The inner tube and outer cylinder were held rigidly apart by means of small glass bridges, C. The condenser fitted loosely into a glass tube, closed at the bottom and provided at the top with a delivery tube, which could be sealed. Platinum

wires from the condenser plates were led out near the top of the wide tube. Connexion with the "live" side of the circuit was made by means of a small wire bridge in mercury cups. The outer cylinder was permanently earthed.

The lower part of the cell was surrounded by a stout copper cylinder, which was earthed, and round which a Dewar flask containing liquid air could be placed. This served to hold the cell, to act as an earthed sheath, and to maintain a uniform temperature in the liquid. Temperature was measured by means of a single-junction copper-constantan thermocouple, with one junction inside the copper sheath and the other in a Dewar flask containing ice and water. The current from it was measured on a microgalvanometer which could be switched out of the valve circuit into the thermocouple circuit.

(c) *Arrangement of circuits.* Oscillatory currents were maintained in circuit  $L_1C_1$  by means of the valve  $V$ , connected as shown. The magnitude of the direct component of the current in the anode circuit is a function of the oscillating currents in  $L_1C_1$ . If a second circuit,  $L_3C_3$ , is now coupled loosely to this, energy is withdrawn when the natural frequency of  $L_3C_3$  is very nearly the same as that in  $L_1C_1$ . If the coupling is adjusted correctly, and the value of  $L_3C_3$  is then altered, the anode current first falls gradually to a well-defined minimum and afterwards rises gradually again; this minimum is very sensitive to change of capacity in  $L_3C_3$ , and could be determined within about 0.02 cm. variation in the capacity of  $C_3$ .

The whole assembly of the apparatus is shown diagrammatically in Fig. 1. The cell and the battery of condensers, denoted by  $C_3$ , were connected in parallel with the inductance,  $L_3$ , which consisted of 12 well-spaced turns of No. 20 copper wire wound on an ebonite former, giving a wave-length of about 200 m.  $L_1$  and  $L_2$  were ordinary wireless inductances, No. 30. The variable condenser,  $C_1$ , had a maximum value of 0.0025 microfarad, and the by-pass condenser,  $C_2$ , had a value of 0.01 microfarad.  $G$  was a microgalvanometer of sensitivity about 0.5 microamp. per scale division.  $R_1$  was a 300-ohm potentiometer, and  $R_2$  a resistance of about 100 ohms.  $R_1$  and  $R_2$  were adjusted so as to neutralise the greater part of the anode current through the galvanometer. A galvanometer shunt,  $R_3$ , was added for convenience of working. The fixed condensers,  $C_{a-d}$ , were calibrated in terms of scale readings on the divided head of  $C_v$ . All the "live" parts of the apparatus, except the experimental cell, were housed in a wooden box with an earthed lining of sheet metal. In order to prevent sudden fluctuations of anode current the valve was wrapped in cotton wool, and a 6-microfarad condenser put across the terminals of the high-tension battery.

Before any measurements were made,  $C_1$  was adjusted so that, with  $C_{a-d}$  in circuit, resonance was obtained with  $C_v$  at about the middle of its range. It then remained unaltered throughout the series of experiments. In an experiment, the resonance point was determined roughly with shunt  $R_3$  partly in, and  $R_1$  adjusted so that the galvanometer needle was about in the centre of the scale at the minimum point.  $R_3$  was then taken out and the minimum found by altering  $C_v$  in each direction three times. The mean of these six readings gave the true resonance point. The experimental cell was then put in circuit and capacity removed from  $C_3$  until resonance was again obtained as before. The capacity of the cell was equal to the capacity removed from  $C_3$ . Another set of readings was then taken to see that the zero had not altered. The change in zero was not usually more than 0.02 unit, whereas the capacity of the cell in air was of the order of 20 units.

(d) *Calibration.* Since the air between the live plate and earth is not replaced completely by liquid, the dielectric constant could not be obtained directly by measuring the ratio of the capacity of the cell when filled and when empty. The cell was therefore calibrated with carbon tetrachloride and chloroform. These liquids were carefully purified and dried; their respective dielectric constants at 25° were taken as 2.20 and 4.79 (Sayce and Briscoe, J., 1926, 2623). The observed capacities were: Air, 30.19;  $CCl_4$ , 57.62;  $CHCl_3$ , 120.31. These were made the basis of a calibration curve for the cell over the range of dielectric constants covered by the experiments.

### Results.

The dielectric constants of sulphur chloride mixtures were measured over the range of compositions from sulphur monochloride to pure chlorine, and at temperatures from that of the room down to that at which solidification was complete. Samples containing less chlorine than the dichloride were put into the cell as equilibrium mixtures; mixtures containing more chlorine were made in the cell and left over-night to reach equilibrium. The observed values for the dielectric constants of 13 different samples at different temperatures are recorded in Table I.

### Discussion of Dielectric Constants.

(a) The dielectric constants of the liquids, which are plotted for 5 typical compositions in Fig. 5, fall as the temperature rises, the relationship being linear in each case. The temperature coefficient, as well as the magnitude of the dielectric constant, rises progressively from chlorine to sulphur monochloride. In accordance with Debye's analysis, this implies that there is a progressive increase in



TABLE I.  
*Dielectric Constants at Various Temperatures.*

50.0 at. % Cl.								
Temp. ....	15.0°	-23°	-41°	-28°	-1°	10.5°	(Solid) *	
ε .....	4.79	5.41	5.81	5.54	5.05	4.88	3.2	
53.18 at. % Cl.				54.8 at. % Cl.				
Temp. ....	14.0°	10.4°	11.0°	-20°	-35.5°	-15.5°	19°	
ε .....	4.39	4.45	4.23	4.65	4.93	4.63	4.14	
58.5 at. % Cl.				63.08 at. % Cl.				
Temp. ...	11.0°	-16.5°	-42.5°	-12.5°	1.6°	15.9°	12.7°	15.9°
ε .....	3.80	4.09	4.49	4.06	3.92	3.28	3.31	3.28
S <sub>2</sub> Cl <sub>2</sub> -Cl <sub>2</sub> mixtures after combination.								
61.39 at. % Cl.			61.84 at. % Cl.		65.24 at. % Cl.			
Temp.	0°		0°		12.5°	-15°	-39.5°	-51° 0°
ε .....	3.61		3.55		3.13	3.34	3.53	3.69 3.27
67.35 at. % Cl.								
Temp. ...	17°	-1°	-46°	-95°	-93°	-79°	-75°	
ε .....	2.96	3.04	3.41	4.58	4.60	4.41	4.36	
Temp. ...	-58.5°	-50°	-32.5°	-25°	-42.5°	-48°	-54° 1°	
ε .....	3.64	3.57	3.34	3.25	3.36	3.45	3.52	3.05
71.53 at. % Cl.								
Temp. ....	-25°	-42.5°	15.2°	13.1°	-16.8°	-46°	-11.8°	8.6°
ε .....	3.02	3.13	2.83	2.83	2.96	3.17	2.96	2.86
76.32 at. % Cl.								
Temp. ....	-7°	-2.3°	8.5°	17.5°	-17°	-30°	-46°	
ε .....	2.77	2.74	2.69	2.64	2.83	2.91	2.99	
Temp. ....	-53.5°	-63.5°	-63°	-62°	-57°	-48°	-40°	
ε .....	3.05	4.23	4.90	5.85	5.99	5.98	5.51	
Temp. ....	-33°	-33°	-33°	-17°	0.4°	21.5°		
ε .....	4.51	4.01	3.81	2.92	2.72	2.61		
85.4 at. % Cl.								
(Solid)*			(Liquid)†					
5.41			2.44					
Chlorine.								
(Solid)*			(Liquid)†		(Solid)*		(Liquid)†	
2.14			2.16		2.07		2.19	

\* Below the temperature of complete solidification.

† A few degrees above the melting point.

the dipole moments as well as in the polarisability of the molecule as atoms of sulphur are inserted between the chlorine atoms in the series  $Cl_2$ ,  $SCl_2$ ,  $S_2Cl_2$ . The curves obtained by plotting the dielectric constants against composition at three temperatures (Fig. 6) are approximately linear, but with a sharp bend at the composition of the dichloride; the absence of a complete discontinuity can be attributed, as in the case of other properties, to the dissociation of the dichloride into a ternary mixture containing also the monochloride and free chlorine. No indication was obtained, however,

FIG. 5.

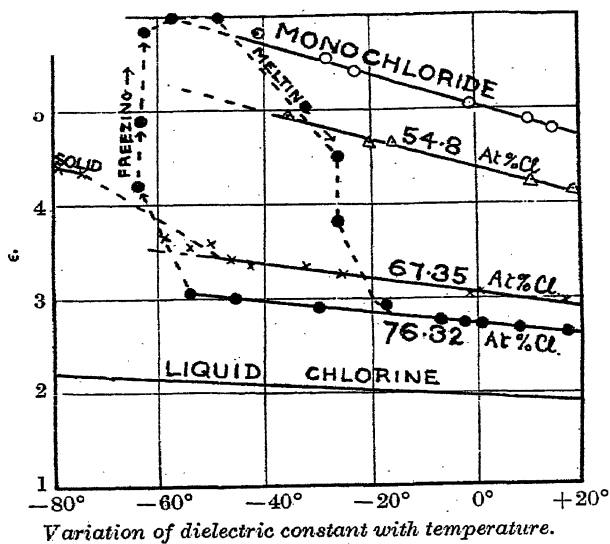
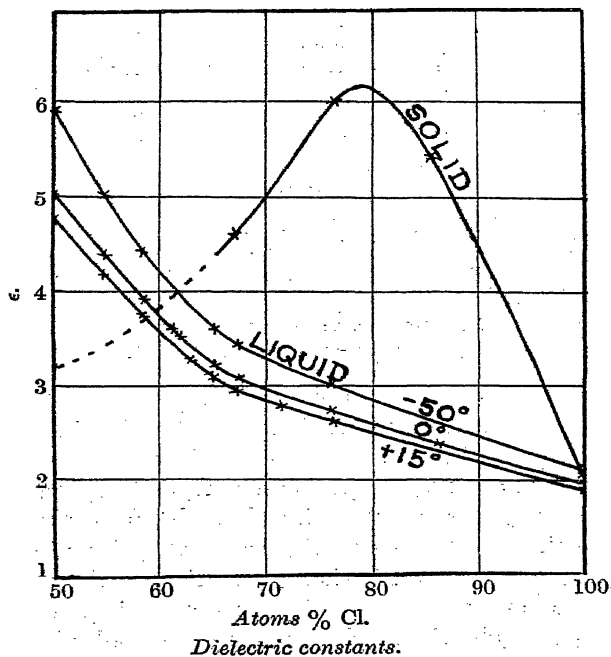


FIG. 6.



of any discontinuity or change of curvature at the composition of the tetrachloride.

(b) The dielectric constants of the solid, which are practically independent of the temperature, have been plotted in Fig. 6 and joined by an arbitrary curve. Three types of behaviour can be recognised.

(i) Solid chlorine, of which the dielectric constant is now recorded, apparently for the first time, has almost exactly the same dielectric constant as liquid chlorine, the average values above and below the m. p. being 2.17 and 2.10. This is interpreted as meaning that, whilst the molecules are polarisable, they have only a very small permanent dipole moment, a result in harmony with the small temperature coefficient recorded above and with other methods of estimating this quantity.

(ii) Sulphur monochloride, on the other hand, after a progressive rise from 4.7 to 5.8 as the liquid is cooled from 15° to -50°, shows an abrupt fall from 6.4 to 3.2 when it finally solidifies. This behaviour is characteristic of liquids with a large permanent dipole moment, since water ( $\epsilon = 81$ ), alcohol ( $\epsilon = 62.7$ ), and nitrobenzene ( $\epsilon = 43.3$ ) show an abrupt fall on solidification to values (3.1, 2.7, and 4.1 respectively) which are comparable with those observed in non-polar liquids such as benzene (2.2) or carbon tetrachloride (2.2).

(iii) An entirely different and novel behaviour was observed in solids of intermediate composition, where a large *increase* of dielectric constant was recorded on solidification. This striking abnormality is shown clearly in the broken curve of Fig. 5, where the dielectric constant is seen to turn sharply upwards as the liquid becomes solid, and to droop again as the solid gradually melts. If we were obliged to admit that the solid had the same chemical constitution as the liquid, we should conclude that the molecules had a negative dipole moment, which is absurd. It is, however, easy to see that this anomaly reaches a maximum *at or near the composition of sulphur tetrachloride*, and must therefore be attributed to the presence of this compound in the solid phase. The proportions in which it would be present in each case cannot yet be stated, and might vary widely with the conditions of crystallisation, but the position of the maximum fixes beyond question the chemical composition of the abnormal component of the mixture. Moreover, the complete dissociation of the tetrachloride on fusion is demonstrated once more by these observations, since, if it survived in any appreciable proportion, it could scarcely fail to reproduce in the curve for the *liquid* the maximum which is so conspicuous a feature of the curve for the *solid* sulphur chlorides. Finally, it may be pointed out that the high dielectric constant (6.2) of solid sulphur

tetrachloride brings it into line with salts such as rock-salt (6.3), sylvine (4.9), fluorspar (6.9), and ammonium chloride (7.0), whereas the solid monochloride (3.2) resembles sulphur (3.9) and chlorine (2.1) in showing the low dielectric constants usually observed in solid molecular compounds.

Since no case appears to have been established previously of a large increase in the dielectric constant of a liquid on solidification,\* it is of interest to record that we have discovered an analogous case in phosphorus pentachloride, m. p. 148°, where our own observations show an increase in the dielectric constant from 2.7 for the liquid at 165° to 4.1 for the solid at 130°. As is well known, Langmuir has attributed to both compounds a salt-like structure, which would explain the high dielectric constant of the solids, but at this stage we are content merely to point out that the abnormality to which we have directed attention suggests a change of structure during the passage from the liquid to the solid state, the precise nature of which awaits investigation with the help of X-ray analysis.

(c) The dielectric polarisation, in terms of the molecular weights ( $M_1$  and  $M_2$ ) and mole-fractions ( $n_1$  and  $n_2$ ) of a mixture, can be deduced from the formula

$$p = \frac{\epsilon - 1}{\epsilon + 2} \frac{M_1 n_1 + M_2 n_2}{d}$$

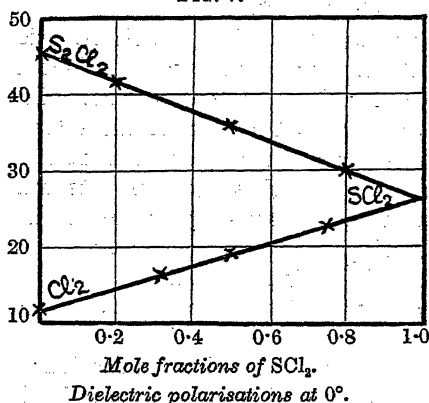
We have therefore calculated the values of this function in the first instance for mixtures of sulphur dichloride (i) with monochloride and (ii) with chlorine, in such large excess that the dissociation of the dichloride would be quite insignificant. Since, however, the formula is not restricted to gases or dilute solutions, we have extended the calculations to solutions containing much larger proportions of the dichloride, and obtained results which are entirely concordant with those given by the more dilute solutions. For this purpose, the dielectric constants were first reduced by interpolation to a temperature of 0°, and were then combined with the densities at this temperature to give the dielectric polarisation of the mixtures. When these numbers are plotted against the mole-fraction of sulphur (Fig. 7), two straight lines are obtained, which intersect accurately on the boundary of the diagram. These liquids therefore obey a simple mixture rule with  $p = 12$ , 27, and 46 for chlorine, dichloride, and monochloride, respectively.

This result might, perhaps, have been predicted if we were certain in advance that we were dealing with a simple ternary (pseudo-binary) system containing only the components shown in the

\* Schmundt, *J. Physical Chem.*, 1904, 8, 122, gives phosphorus (solid) 4.1, (supercooled liquid) 3.85 at 20°; Pirani, *Diss.*, Berlin, 1903, gives sulphur (at f. p.) 3.98, solid (room temperature) 4.22.

equation  $\text{Cl}_2 + \text{S}_2\text{Cl}_2 \rightleftharpoons 2\text{SCl}_2$ . If, however, we were to postulate, with Trautz (*Z. Elektrochem.*, 1929, **35**, 110), a series of equilibria in which the tetrachloride plays an essential part, no such simple relationship could be expected. The data plotted in Fig. 7 are therefore of real importance, since they prove that the compound formed by adding a small excess of chlorine to sulphur monochloride (which might have been  $\text{S}_3\text{Cl}_4$ ) and the compound formed by adding a small amount of sulphur to pure liquid chlorine (generally supposed hitherto to be  $\text{SCl}_4$ ) have in fact the same constant of dielectric polarisation, and in this respect, as in others, are identical.

FIG. 7.



#### Conductivities.

It is generally agreed that sulphur mono- and di-chlorides and chlorine are covalent compounds, as represented by the formulæ  $\text{Cl-S-S-Cl}$ ,  $\text{Cl-S-Cl}$ , and  $\text{Cl-Cl}$ ; and this formulation is confirmed by the gradation in the dielectric polarisation of the three substances. Langmuir, however, has attributed to sulphur tetrachloride a polar formula  $[\text{SCl}_3]^+\text{Cl}^-$ , and the electronic theory of valency suggests that a similar polar formula should be assigned to trisulphur tetrachloride,

which may be formulated as  $[\text{ClS-}\overset{+}{\text{S}}\text{Cl-S-Cl}]\text{Cl}^-$ . Evidence of the presence of sulphur tetrachloride and justification of Langmuir's polar formula would therefore be provided simultaneously if solutions could be prepared showing a substantial electrolytic conductivity. The apparatus used to test this is shown in Fig. 4. It had a cell constant of 0.17 and was specially designed for use at low temperatures with corrosive substances easily decomposed by water.

(i) A solution of sulphur tetrachloride (*sic*) in liquid chlorine was prepared by weighing the liquid dichloride into the cell, cooling it over liquid air, and passing in an excess of chlorine. When the

liquid was cooled to a temperature at which solid sulphur tetrachloride was beginning to separate, the conductivity of the saturated solution was found to be only  $0.18 \times 10^{-6}$  mho, i.e., of the same order as that of liquid chlorine.

(ii) A solution of sulphur dichloride in liquid hydrogen chloride was prepared by weighing the liquid dichloride into the cell and condensing hydrogen chloride by cooling over liquid air. The conductivity of the solution just below its boiling point was  $0.7 \times 10^{-6}$  mho. Chlorine was then passed in until the red colour of the dichloride had disappeared completely by precipitation of the tetrachloride as a colourless solid. The conductivity of the saturated solution was then  $0.65 \times 10^{-6}$ .

These observations show that no electrolytic conductivity is developed on attempting to prepare solutions of sulphur tetrachloride in chlorine or in hydrogen chloride. This result could be interpreted as showing either (i) that the tetrachloride is a non-electrolyte in these two solvents, or (ii) that it is insoluble in, or completely dissociated by, these two solvents and is therefore precipitated quantitatively as fast as it is formed. There is no method available for distinguishing sharply between these possibilities, although the first deduction is obviously unproven in view of the failure of all attempts to detect the presence of the tetrachloride in solution. The completeness with which the tetrachloride is removed from the solutions is, however, itself an indication of a wide difference in polarity from chlorine and the mono- and di-chloride, with which it should otherwise be freely miscible, as in the case of the non-polar chlorides of carbon. A similar argument can be applied to trisulphur tetrachloride which, at temperatures below  $-100^{\circ}$ , forms two liquid layers with its products of dissociation. We can therefore only return a negative reply to any questions as to the conductivity or other similar properties of sulphur tetrachloride, since we have been unable to find any evidence of the existence of this compound in the liquid state.

#### *Summary.*

(a) The dielectric constants of sulphur chloride mixtures have been measured over the range of composition from monochloride to chlorine and from room temperature down to the freezing points.

(b) The isothermals for the liquids confirm the existence of sulphur dichloride, but do not show any inflexion corresponding with the tetrachloride, even at  $-50^{\circ}$ .

(c) The dielectric constant of the solids shows a pronounced maximum at the composition of the tetrachloride.

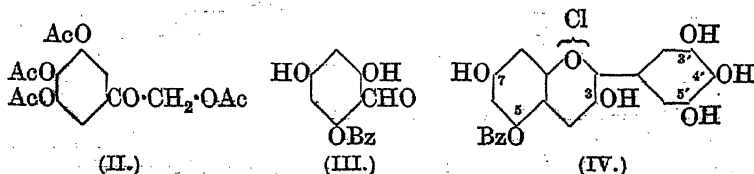
CVII.—*A Synthesis of Pyrylium Salts of Anthocyanidin Type. Part XIX. A Synthesis of Delphinidin Chloride not involving a Demethylation Process, and Syntheses of Hirsutidin Chloride and of Delphinidin Chloride 3'-Methyl Ether, possibly identical with Petunidin Chloride.*

By WILLIAM BRADLEY, ROBERT ROBINSON, and GEROLD SCHWARZENBACH.

THE recognition that the purest specimens of cyanidin chloride can most readily be obtained if demethylation of methyl ethers is entirely avoided (Robertson and Robinson, Part XV, J., 1928, 1526; Willstätter and Robinson, *Ber.*, 1928, 61, 2504) made it desirable that the improved synthetical method already applied to the cases of pelargonidin chloride (Robertson, Robinson, and Sugiura, Part XVI, J., 1928, 1533) and cyanidin chloride (Part XV, *loc. cit.*) should be extended to include the preparation of delphinidin chloride.

This has now been carried out, and the resulting hexahydroxy-flavylium chloride compared with a specimen of delphinidin chloride from a natural source, no divergences of behaviour of the specimens being detected.

*O*-Triacetylgalloyl chloride and diazomethane furnished  $\omega$ -*diaz*-3:4:5-*triacetoxyacetophenone*,  $(\text{AcO})_3\text{C}_6\text{H}_2\cdot\text{CO}\cdot\text{CHN}_2$  (I), and  $\omega$ :3:4:5-*tetra-acetoxyacetophenone* (II) was readily obtained from the *diaz*-derivative by the action of acetic acid.



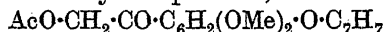
The tetra-acetate (II) condensed with 2-*O*-benzoylphloroglucin-aldehyde (III) (Robertson and Robinson, J., 1927, 1710) in alcohol-ethyl acetate solution under the influence of hydrogen chloride, with production of 5-*O*-benzoyldelphinidin chloride (IV), the acetyl groups being all removed in the course of the reaction. The final stage, namely, the elimination of the benzoyl group, gave trouble owing to the oxidisability of the substance in alkaline solution, but this difficulty was not insuperable. The debenzoylated product of the action of aqueous-alcoholic sodium hydroxide on (IV) was changed

to delphinidin chloride by treatment with hydrochloric acid under special conditions which it was found necessary to observe closely.

*Synthesis of Hirsutidin Chloride.*—In 1927, Karrer and Widmer (*Helv. Chim. Acta*, 1927, **10**, 758) isolated a new anthocyanin, hirsutin chloride, from the *Primula hirsuta*, and found that, on hydrolysis in the usual manner, *hirsutidin chloride*,  $C_{18}H_{17}O_7Cl$ , was obtained.

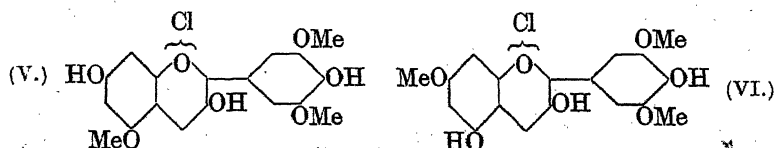
This anthocyanidin contained three methoxyl groups, gave syringic acid on oxidation and delphinidin salts on demethylation, and was therefore recognised as a methyl ether of syringidin chloride (*O*-methylmalvidin chloride). The methyl groups might be in the 3:3':5', 5:3':5', or 7:3':5'-positions, and, of these, Karrer and his collaborators preferred the last two. The synthesis of *O*-3:3':5'-trimethyldelphinidin chloride has already been effected (Bradley and Robinson, J., 1928, 1541), and, since the properties of this salt were different from those of hirsutidin chloride, concurrence with Karrer's view was expressed.

5:3':5'-*O*-Trimethyldelphinidin chloride (V) was obtained by condensing 2-*O*-methylphloroglucinaldehyde with  $\omega$ -acetoxy-4-benzoyloxy-3:5-dimethoxyacetophenone,



(Bradley and Robinson, *loc. cit.*), in formic acid solution in presence of hydrogen chloride. As in the synthesis of malvidin chloride, the benzyl group is eliminated.

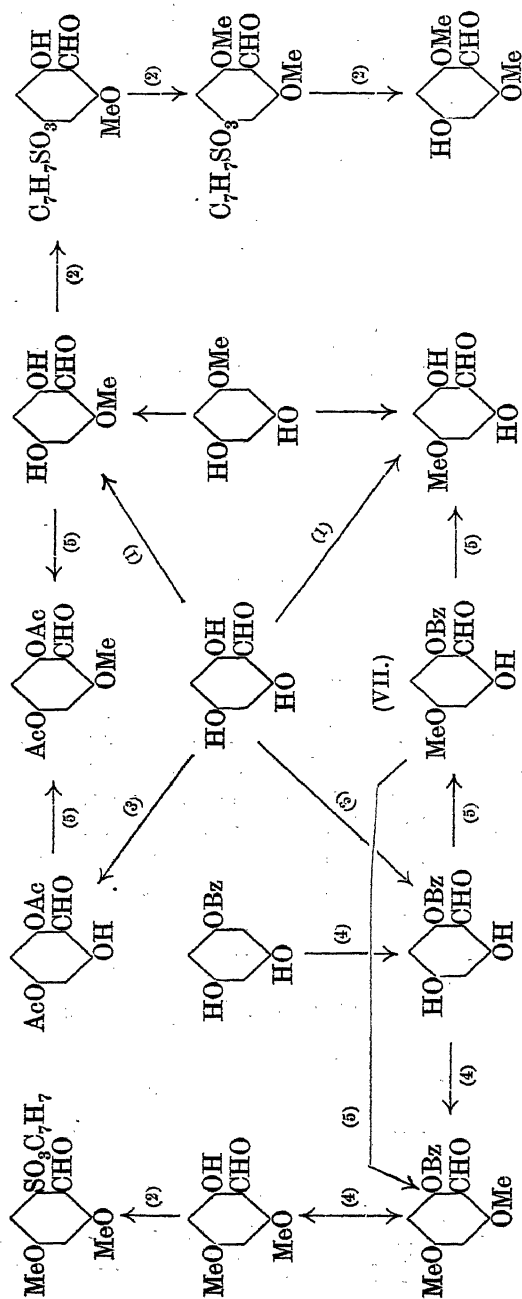
7:3':5'-*O*-Trimethyldelphinidin chloride (VI) was obtained by hydrolysing its 5-*O*-benzoyl derivative derived from the use of



2-*O*-benzoyl-4-*O*-methylphloroglucinaldehyde (VII) in a similar process. This salt proved to be identical with hirsutidin chloride. The aldehyde (VII) was obtained on methylating 2-*O*-benzoylphloroglucinaldehyde by means of silver oxide and methyl iodide; its constitution follows from the occurrence of the flavylum salt synthesis and from relations represented in the subjoined scheme.

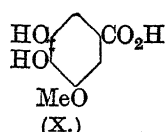
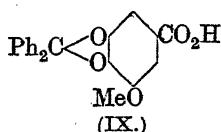
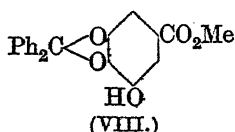
*Synthesis of Delphinidin Chloride 3'-Methyl Ether.*—This substance, which may be identical with petunidin chloride (Willstätter and Burdick, *Annalen*, 1916, **412**, 217), has been synthesised by an application of the *O*-benzoylphloroglucinaldehyde method; the chief difficulties were encountered in obtaining the required ketonic component.





(1) Karrer and Bloch, *Helv. Chim. Acta*, 1927, 10, 374; (2) Karrer and Helfenstein, *ibid.*, p. 789; (3) Robertson and Robinson, J., 1927, 1710; (4) Robertson, Robinson, and Struthers, J., 1928, 1455; (5) this paper.

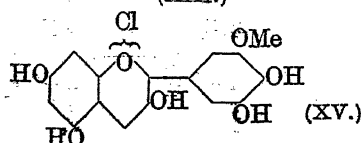
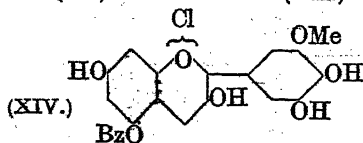
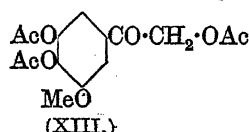
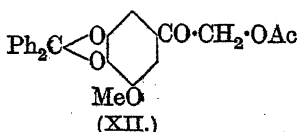
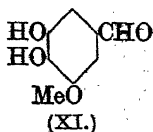
The first step was to devise a more convenient method for the preparation of 3-*O*-methylgallic acid than those recorded by Vogl (*Monatsh.*, 1899, **20**, 397) and Fischer (*Ber.*, 1913, **46**, 1123). In this, we were successful, and the new method of protection of vicinal hydroxyl groups in polyhydric phenols that was adopted is one that should find numerous applications in other directions. Methyl gallate and diphenyldichloromethane in acetone solution in presence of pyridine, with subsequent addition of sodium hydroxide, afforded methyl 3-hydroxy-4:5-diphenylmethylenedioxybenzoate (VIII). This ester was methylated by means of methyl iodide and sodium ethoxide, and, on hydrolysis by alkaline solutions, 3-methoxy-4:5-diphenylmethylenedioxybenzoic acid (IX) was obtained; 3-*O*-methylgallic acid (X) resulted when the methylated ester was treated with boiling concentrated hydrochloric acid.



3-*O*-Methylgallic acid had m. p. 220° (diacetyl derivative, m. p. 170—171°) in agreement with the description of Fischer (*loc. cit.*) (Vogl, *loc. cit.*, gives the m. p. 199—200°).

Shriner and McCutchan, however, in a recent paper (*J. Amer. Chem. Soc.*, 1929, **51**, 2193), have stated that the acid has m. p. 132° (diacetyl derivative, m. p. 102—103°), and it was therefore necessary to explain this discrepancy. We find that the action of 8% aqueous sodium hydroxide at 200° on bromovanillin in the presence of copper actually yields 3-*O*-methylgallaldehyde (XI) and not the corresponding acid, as Shriner and McCutchan supposed.

Starting with the diphenylmethyle ether or the diacetyl derivative of 3-*O*-methylgallic acid and passing through the stages  $R\cdot CO_2H$ ,  $R\cdot COCl$  and  $R\cdot CO\cdot CHN_2$  to  $R\cdot CO\cdot CH_2\cdot OAc$ , we obtained the  $\omega$ -acetoxygallacetophenone derivatives (XII) and (XIII), respectively, and either of these, on condensation with 2-*O*-benzoyl-



phloroglucinaldehyde in the usual way, gave rise to 5-*O*-benzoyl-3'-*O*-methyldephinidin chloride (XIV). The 3'-*O*-methyldephinidin chloride (XV) obtained on hydrolysis very closely resembles petunidin chloride, but we are unable to express any opinion at this stage on the question of its identity with that anthocyanidin.

#### EXPERIMENTAL.

$\omega$ -Diazo-3:4:5-triacetoxyacetophenone (I).—Triacetylgalloyl chloride was prepared by the method of Fischer, Bergmann, and Lipschitz (*Ber.*, 1918, 51, 55). A solution of the chloride (18 g.) in chloroform (50 c.c.) was added during 10 minutes to ethereal diazomethane (140 c.c., from 25 c.c. of nitrosomethylurethane) cooled to  $-10^{\circ}$ . Evolution of nitrogen accompanied the rapid separation of pale yellow crystals of the diazo-ketone, and these were collected after 30 minutes and washed with ether (yield, 17.6 g.; m. p.  $120-122^{\circ}$ ). For analysis, the diazo-ketone was crystallised twice from benzene; it was obtained in stout lemon-yellow plates or tables, m. p.  $125-126^{\circ}$  with evolution of nitrogen (Found: C, 52.7; H, 3.7; N, 8.7, 8.8.  $C_{14}H_{12}O_7N_2$  requires C, 52.5; H, 3.8; N, 8.7%).

$\omega$ -Diazo-3:4:5-triacetoxyacetophenone is easily soluble in alcohol and benzene, more sparingly soluble in ether, and almost insoluble in light petroleum. It possesses the usual properties of diazomethylketones. Nitrogen is eliminated by heating, by the addition of iodine or aqueous mineral acids to an alcoholic solution, or by warming with glacial acetic acid. A drop of aqueous sodium hydroxide added to the cold dilute alcoholic solution causes the development of a yellow colour; from more concentrated solutions, a green amorphous solid, soluble in water, is precipitated, and, when gently heated, these solutions become reddish-brown.

$\omega$ :3:4:5-Tetra-acetoxyacetophenone (II).—A solution of the diazo-ketone (12 g.) in pure glacial acetic acid (25 c.c.) was warmed at  $60-80^{\circ}$  until the vigorous evolution of nitrogen had ceased (about 30 mins.). The cooled solution was diluted with ether (300 c.c.), and the crystalline precipitate of  $\omega$ :3:4:5-tetra-acetoxyacetophenone collected (yield, 9.3 g.; m. p.  $118-121^{\circ}$ ). The ethereal mother-liquor was washed with potassium bicarbonate solution, filtered, dried, and evaporated; an oil (2 g.) remained which gave a bluish-green coloration with ferric chloride, and from which only a small amount of the crystalline ketone could be isolated. The proportion of the oily fraction was greater when less pure acetic acid was employed and was increased, also, by more prolonged heating during the decomposition of the diazo-ketone. When the ketone was isolated by pouring the cooled acetic acid solution into water, the oily product could not be employed directly, and, after recrystallisation, the

yield was considerably smaller than that obtained by the above procedure. The ketone crystallised from ethyl alcohol (charcoal) in tables or colourless thick plates having a characteristic spearhead form, m. p. 122—123° (Found: C, 54.9; H, 4.8.  $C_{16}H_{16}O_9$  requires C, 54.6; H, 4.6%).

$\omega : 3 : 4 : 5$ -Tetra-acetoxyacetophenone is readily soluble in alcohol, benzene and acetic acid, but more sparingly soluble in ether. It is insoluble in aqueous sodium carbonate, although rapidly dissolved by cold dilute sodium hydroxide solution. An alcoholic solution gives no reaction with ferric chloride, and the ketone reduces Fehling's solution in the cold.

*Benzoyldelphinidin Chloride* (IV) (First preparation).—Finely powdered  $\omega : 3 : 4 : 5$ -tetra-acetoxyacetophenone (5.2 g.) and benzoylphloroglucinaldehyde (4.0 g.) were added to a mixture of ethyl alcohol (80 c.c.) and ethyl acetate (80 c.c.), and the solution cooled to 0°. Dry hydrogen chloride was admitted and, saturation having been attained, the mixture was allowed to reach the room temperature. At first, a portion of the aldehyde was precipitated, but later redissolved completely. After being kept over-night, the dark green flavylum salt was collected and washed with ether (yield, 2 g.). The use of ethyl alcohol alone gave an amorphous product; ethyl acetate alone furnished a crystalline substance which gave no coloration with ferric chloride in alcoholic solution. The product was obtained in short prisms, having in mass a dark olive-green appearance. It was recrystallised from hot methyl alcohol (20 vols.) containing concentrated hydrochloric acid (1 vol.), in which it was only very sparingly soluble. The recrystallised material was dull greyish-violet in appearance and consisted of slender, dark red prisms.

Benzoyldelphinidin chloride is easily soluble in alcohol to a violet-red solution; the violet shade increases on keeping or on dilution with more alcohol; the very dilute solution in methyl alcohol is pure blue. When an equal volume of water is added to the violet-red methyl-alcoholic solution, the colour fades instantly to pale blue, and the red colour is immediately restored on the addition of acid. Heated with 0.5% hydrochloric acid, the salt dissolves to a pale red solution which rapidly fades even while in contact with the undissolved substance. A pale blue colour results when a drop of aqueous sodium carbonate is added to a freshly prepared alcoholic solution of the salt; on dilution with water, the solution becomes green and then rapidly fades to yellow. A drop of 5% aqueous potassium hydroxide added to the alcoholic solution gives a bluish-green colour which fades slowly to green; on the other hand, a drop of 0.5% potassium hydroxide gives a fairly stable, pure blue colour

which is still weakly blue after one hour. Similarly, solid sodium acetate added to the freshly prepared methyl-alcoholic solution gives a fairly stable, pure blue colour. The salt dissolves in aqueous sodium carbonate, but the blue colour initially produced fades almost immediately to violet.

*Delphinidin Chloride* (First preparation).—Finely powdered, crude benzoyldelphinidin chloride (2 g.) was added to 10% aqueous sodium hydroxide (16 c.c.) from which air had been displaced by a stream of hydrogen, and the solution kept 4 hours after the salt had dissolved completely. The deep blue solution formed initially changed through green to orange. Ethyl alcohol (10 c.c.) and concentrated hydrochloric acid (10 c.c.) were then added, and the deep red solution was kept in the cold during 3—4 days until a portion dissolved in aqueous sodium carbonate with a pure blue colour. Attempts to hasten the re-synthesis of the flavylum salt by warming the solution or by increasing the concentration of acid gave oily products from which crystalline material could not be obtained. Concentrated hydrochloric acid (30 c.c.) was then added in several small portions, and, next day, almost the whole of the product had separated in a microcrystalline condition. Washed with hydrochloric acid and dried in the air, it formed a dense, dark brownish-red powder, having a greenish lustre.

Preliminary purification was effected by solution in a small volume of ethyl alcohol and precipitation of the salt from the filtered solution by means of concentrated hydrochloric acid. The flocculent material was collected, dried, and washed with ether (Specimen A). The product was obtained in an oily condition when precipitation was effected from an alcoholic hydrogen chloride solution by the addition of ether.

Specimen A separated completely from solution in 15% hydrochloric acid, but several repetitions of this treatment failed to give definitely crystalline material. When dry hydrogen chloride was admitted above the surface of a concentrated alcoholic solution of Specimen A cooled in ice-water, crystalline material was readily obtained in small yield as an olive-green lustrous substance. The mother-liquor could be almost completely precipitated by dilution with aqueous hydrochloric acid, but the material (an ethyl ether?) obtained in this way was much more sparingly soluble than delphinidin chloride. Attempts to obtain delphinidin chloride tetrahydrate from the crystalline portion under the conditions of Willstätter and Weil (*Annalen*, 1916, 412, 190) were unsuccessful.

When, however, Specimen A was heated with hydriodic acid under Zeisel conditions, as described by Willstätter and Weil (*loc. cit.*), delphinidin iodide separated in a well-crystallised condition,

although in small yield. The crystal form, pointed plates, was identical with that of the specimen from material of natural origin. Willstätter and Weil remark that the crude anthocyanidin obtained from the glucoside could not be crystallised from methyl-alcoholic hydrogen chloride, but the crystalline iodide was readily obtained and from this the crystalline chloride. The iodide was obtained in better yield by dissolving Specimen A (1.15 g.) in cold 0.5% hydrochloric acid (30 c.c.) and adding freshly distilled hydriodic acid (15 c.c., b. p. 127°) to the filtered solution. A small amount of crystalline material was precipitated rapidly, but the crystallisation was complete only after several days, during which the containing flask was filled with carbon dioxide and kept in the dark. The crystals were collected, washed with a little dilute hydriodic acid, dried in the air, and washed with ether (yield, 0.45 g.). Only a very small additional amount was obtained when the mother-liquor was concentrated. The iodide was obtained in this manner in stout prisms or tables, green in mass and having a bright yellow lustre. This salt crystallises from its solution in hot dilute hydriodic acid on the addition of concentrated hydriodic acid in well-shaped, elongated rhombic plates, often connected by their acute-angled corners so as to form rosettes. The crystals are deep red by transmitted light and exhibit a marked yellow glitter. The same crystal shape and appearance have been noted in material of natural origin (demethylation of natural malvidin).

The crude crystalline iodide (0.95 g.) was dissolved in 0.5% hydrochloric acid (30 c.c.), and the chloride precipitated by adding concentrated hydrochloric acid (30 c.c.) to the filtered solution. The amorphous chloride, which separated at once and completely, was crystallised by dissolving 0.13 g. in 5% hydrochloric acid (9 c.c.) and adding hot concentrated hydrochloric acid (18 c.c.) to the hot solution. The chloride separated on cooling in long, dark red prisms or in crystalline granules. The former were green by reflected light and had a bright yellow lustre. Two recrystallisations were effected under the same conditions (Specimen B) (Found: C, 48.3; H, 4.0; Cl, 9.2; loss at 110° in a high vacuum, 9.3. Found in anhydrous material: C, 53.4; H, 3.2; Cl, 10.1.  $C_{15}H_{11}O_7Cl \cdot 2H_2O$  requires C, 48.1; H, 4.0; Cl, 9.5;  $H_2O$ , 9.6%.  $C_{15}H_{11}O_7Cl$  requires C, 53.2; H, 3.3; Cl, 10.5%).

*Benzoyldelphinidin Chloride* (Second preparation).—Numerous further experiments on the conditions for the preparation of this salt were carried out. The product obtained by condensation of the components in ether-alcohol was not homogeneous and the yield was inferior; a very considerable improvement followed on the adoption of the following method.

2-*O*-Benzoylphloroglucinaldehyde (7.4 g.) and  $\omega$ :3:4:5-tetra-acetoxyacetophenone (9.6 g.), along with ethyl alcohol (150 c.c.), were mixed in a flask provided with an efficient stirrer, a tap funnel, inlet and outlet (calcium-chloride tube) tubes, and cooled in melting ice. The mixture was saturated with hydrogen chloride and, after 2 hours, was warmed at 30° for 1½ hours; it was then again cooled to near 0°, and acetyl chloride (167 c.c.) gradually introduced. The process was interrupted for 3 hours when about half of the acetyl chloride had been added. The product was collected (8.2 g.) after about 12 hours. Altogether, 22.6 g. of the salt were obtained from six experiments in which the conditions were slightly modified; cooling at 0° during the whole period greatly diminished the yield, but substituting the room temperature for the 30° mentioned above gave good results (1.9 g. from 2 g. of the aldehyde and 6.4 g. from 6 g.). It was now found that *benzoyldelphinidin chloride* could be crystallised, by adding concentrated hydrochloric acid to its solution in ethyl alcohol, in prisms forming a glistening green mass (Found in material dried over sulphuric acid: C, 57.6; H, 3.7.  $C_{22}H_{15}O_8Cl \cdot H_2O$  requires C, 57.4; H, 3.7%).

*Delphinidin Chloride* (Second preparation).—After a preliminary test, 20 g. of the crude benzoyl compound prepared by the acetyl chloride method were hydrolysed in five similar experiments as follows:—

The finely powdered benzoyl compound (4.0 g.) was added to 10% aqueous sodium hydroxide (30 c.c.), cooled in ice and frequently shaken until dissolution was complete (15 mins.). Air was previously displaced from the apparatus by hydrogen, and a current of the latter was passed through the alkaline solution during the hydrolysis. After 15 minutes, the solution was allowed to reach the room temperature, and, after 3½ hours, an ice-cold mixture of ethyl alcohol (20 c.c.) and concentrated hydrochloric acid (20 c.c.) was added. The clear, deep red solution was kept 10–12 days until a portion gave a pure blue coloration with a little sodium carbonate solution; the time required for the completion of this stage was considerably longer than the corresponding period for the earlier preparation. Concentrated hydrochloric acid (120 c.c.) was then added in several portions, the solution kept over-night, and the precipitated mixture of salts and benzoic acid collected, washed with 20% hydrochloric acid, and dried (Y).

The united filtrates gave, on keeping, a further crop of the flavylum salt (Z; yield, 3.15 g.), which was almost free from benzoic acid and inorganic salts and for this reason was conveniently worked up separately.

The united first fractions Y were dried in the air, finely powdered, and washed with ether; when wet with the solvent, the material

became pasty, but friable again immediately the solvent had evaporated. After being powdered again, the product was extracted with cold ethyl alcohol-concentrated hydrochloric acid (in all, EtOH, 120 c.c.; 30% HCl, 30 c.c.): there was a considerable residue (R) (see below). The filtered extracts were mixed with an equal volume of water and with concentrated hydrochloric acid (250 c.c.). The amorphous product was collected and extracted with cold 0.5% hydrochloric acid (about 500 c.c. in several portions and with mechanical stirring). Almost the whole of the substance dissolved, and it was recovered by the addition of concentrated hydrochloric acid (1300 c.c.) to the filtered solution so as to make the final hydrogen chloride concentration about 25%. When the precipitate was collected, dissolved in hot 0.5% hydrochloric acid, and freshly distilled hydriodic acid (80 c.c., *d* 1.7) added to the filtered solution, the iodide slowly separated during several days in a beautifully crystalline condition. The usual precautions—protection from light and replacement of the air of the containing flask by carbon dioxide—were observed.

The fraction Z of the crude chloride was treated in a very similar fashion, the iodides from Y and Z were united and dissolved in hot 5% hydrochloric acid (400 c.c.), and the chloride was precipitated by the addition of concentrated hydrochloric acid (600 c.c.). This product was amorphous, but crystallised by repetition of the solution in 5% hydrochloric acid and increase of the acid concentration to 25% (Specimen C) (Found in air-dried material: C, 48.5; H, 3.9; loss at 110° in a high vacuum, 9.0. Found in anhydrous material: C, 53.3; H, 3.1%).

The crystals of this specimen were deep red prisms by transmitted light and olive-green in mass; under some conditions, which it is not possible to define precisely, the material separated in ill-defined granules, and occasionally as opaque aggregates, from which well-shaped crystals appeared to protrude.

The residue R (above) crystallised directly from methyl alcohol-hydrochloric acid (9 vols. CH<sub>3</sub>OH and 1 vol. 30% hydrochloric acid) (Specimen D), and the material recovered from the mother-liquor was crystallised in the usual way from 25% hydrochloric acid (Specimen E). Subsequent to these experiments, it was found that less difficulty was experienced in crystallising the delphinidin chloride, made substantially as described, if the hydrogen used to displace air from the apparatus during the hydrolysis was freed from traces of oxygen by passage through an alkaline pyrogallol solution.

The specimens B, C, D and E exhibited identical colour reactions, and these were, further, identical with those of specimens of delphinidin chloride prepared by demethylation of malvidin



(syringidin) chloride and by the hydrolysis of vicin picrate with hydrochloric acid. We are greatly indebted to Professor P. Karrer for kindly supplying the delphinidin chloride (*ex malvidin*) and the vicin picrate. Vicin is an anthocyanin of the sweet pea (Karrer and Widmer, *Helv. Chim. Acta*, 1927, **10**, 67) and is a delphinidin glucoside.

The colours observed in a range of buffered solutions of definite  $p_H$  under the conditions prescribed by Robertson and Robinson (*Biochem. J.*, 1929, **23**, 35) were the following, the observations in parentheses referring to 5-*O*-benzoyldelphinidin chloride.

1% Hydrochloric acid, red with blue tinge (rose red, bluer than delphinidin and partly precipitated on standing), unchanged after 15 minutes; 10% hydrochloric acid, the same (similar, but all the salt was precipitated, leaving a colourless solution); (1) permanganate (purplish-red, fading to violet); (2) similar, but shade bluer [similar to (1)]; (3) similar to (2) (no change); (4) not much change, violet-red (deeper violet); (5) deeper violet-red (deeper violet); (6) similar reddish-violet (bluer violet); (7) reddish-violet (violet-blue); (8) reddish-violet, bluer in thin layers (blue); (9) blue in thin layers, violet in thick layers (blue); (10) blue (blue with no violet tinge); (11) rather dull greenish-blue (blue); (12), (13) and (14), no change [(14) and (15) are greener and duller]; (15) similar colour, quickly becoming slate blue and then very pale brown.

After 15–20 minutes, the colours observed were: (1) faded rose pink (very weak violet); (2) and (3) weak violet [(2), (3) and (4) form a series in which a reddish-violet colour increased]; (4) a little more intense reddish-violet; (5) and (6) more intense reddish-violet; (7) bluer violet; (8) weaker blue-violet; (9)–(13) inclusive, greenish-blue [(5), (6), (7), (8) and (9) form a series in which the violet colour becomes bluer; (10), (11) and (12) blue; (13) bluish-green]; (14) weak, faded green (pale green); (15) yellowish-brown (pale brownish-yellow).

After 1½ hours, the colours were: (1), (2) and (3), weak violet, increasing in (4), (5) and (6), bluer in (7) and violet-blue in (8); (9), (10), and (11) were green, tinged with blue; (12), (13), (14) and (15), yellowish-brown [all faded; (1), (2), (3) and (4), increasing weak violet; (5), (6), (7) and (8), bluer; (9), (10) and (11), blue; (12), bluish-green; (13), pale green; (14) and (15), pale brownish-yellow].

After 24 hours, (1), (2), (3), (4) and (5), practically colourless, with a small, flocculent, violet precipitate; (6) very faint violet, no flocks; (7) and (8), almost colourless; (9) very faint yellow; (10), (11), (12), (13) and (14), yellow, increasing in intensity to weak golden-yellow; (15), weaker yellow [(1), very faintly blue, a trace of violet flocculent precipitate; (2) and (3), faintly blue, a little more pre-

cipitate; (4) and (5) weak blue, maximum precipitation; (6) and (7), weak blue; (8), very pale blue, no precipitate; (9) and (10), almost colourless; (11), (12), (13), (14), (15), (16) and (17), weak lemon-yellow].

The comparisons of the different specimens of delphinidin chloride, natural and synthetic, disclosed no divergences whatever, either in regard to the shades of colour observed, the relative amounts of precipitates or the rate of change of the colours of the solutions. The specimens (B), (C), (D) and (E) had all the ordinary properties of delphinidin chloride as recorded by Willstätter and his collaborators, and specimen (D) was used for the preparation of the characteristic monohydrate under the conditions prescribed by Willstätter and Weil (*Annalen*, 1916, 442, 192). The experiment succeeded, and well-shaped, dark brownish-violet, rhombic plates, all of them elongated, as shown in some cases in Willstätter and Weil's figure, were obtained (Found: loss at 110° in a vacuum, 6.0.  $C_{15}H_{11}O_7Cl \cdot H_2O$  requires  $H_2O$ , 4.9%). The somewhat high value for the loss in weight may be due to loss of hydrogen chloride or to admixture with one of the other hydrates, but it is interesting to note that Willstätter and Weil (*loc. cit.*) found the loss in a vacuum desiccator to be 5.88% and 5.57% in two experiments.

The crystals of the monohydrate exhibited the behaviour towards 5% hydrochloric acid which was described by Willstätter and Weil in the case of the specimen of natural origin.

6-Hydroxy-2-benzoyloxy-4-methoxybenzaldehyde (VII).—The preparation of a monomethyl ether of *O*-benzoylphloroglucinaldehyde was unsuccessfully attempted in several different ways, using methyl iodide and alkali-metal salts of the hydroxy-aldehyde, but the following process gave moderately satisfactory results.

A mixture of *O*-benzoylphloroglucinaldehyde (2.5 g.), methyl iodide (4.1 g.), finely divided silver oxide (3.3 g.), and acetone (25 c.c.) was mechanically shaken for 12 hours, filtered, and the precipitate washed with acetone. The pale yellow filtrates were united and the solvent was removed under reduced pressure. The orange-yellow viscous residue was dissolved in ether (50 c.c.), filtered from a trace of insoluble flocculent material, and washed with 10% aqueous sodium carbonate. Acidified, this fraction gave only a negligible amount of a colourless crystalline substance, although *O*-benzoylphloroglucinaldehyde is readily removed from its solution in ether by this means. The ethereal solution was then twice shaken with 5% aqueous potassium hydroxide (10 c.c., 5 c.c.) and the alkaline solutions were separated and acidified with dilute acetic acid, without delay. This product was a pink crystalline precipitate and a colourless emulsion, which became resolved into a

mass of fine needles in the course of 4—5 hours; yield, 1.9 g., m. p. 95—102°. The ethereal solution was again washed with 5% potassium hydroxide solution, dilute sulphuric acid, and water; dried and evaporated, it gave an oily solid (0.23 g.) which consisted essentially of benzoyldimethylphloroglucinaldehyde (Robertson, Robinson, and Struthers, J., 1928, 1455).

In a second experiment, *O*-benzoylphloroglucinaldehyde (5.2 g.) and methyl iodide (4.6 g.) in acetone (40 c.c.) were shaken with silver oxide (3.5 g.) during 5 hours, after which methyl iodide (4.6 g.) in acetone (10 c.c.) and silver oxide (3.5 g.) were added and the shaking was continued over-night. Benzoyldimethylphloroglucinaldehyde (2.2 g., m. p. 143—145°) and benzoylmethylphloroglucinaldehyde (1.5 g.) were isolated.

*6-Hydroxy-2-benzoyloxy-4-methoxybenzaldehyde* crystallised from ethyl alcohol in colourless plates, m. p. 109° (Found: C, 66.0; H, 4.5.  $C_{15}H_{12}O_5$  requires C, 66.2; H, 4.4%), easily soluble in benzene and chloroform, very sparingly soluble in light petroleum and insoluble in water. The alcoholic solution gives a brownish-red coloration with ferric chloride. A solution of the aldehyde (1.8 g.) in cold 10% aqueous sodium hydroxide (10 c.c.) was kept in an atmosphere of hydrogen (probably unnecessary) during 4 hours. The acidified solution was extracted with ether, and the extract was washed with aqueous potassium bicarbonate, in order to remove benzoic acid, then with water, dried, and evaporated. The colourless residue crystallised from benzene in slender needles, m. p. 141—142°, unchanged by further recrystallisation from water.

This aldehyde is identical with phloroglucinaldehyde 4-methyl ether, isolated by Karrer and Bloch (*Helv. Chim. Acta*, 1927, 10, 374) from the product of methylation of phloroglucinaldehyde by diazomethane, and from the mixture of aldehydes obtained from *O*-monomethylphloroglucinol by the Gattermann reaction. We were able to confirm this by direct comparison with a specimen of the substance kindly sent to us by Professor Karrer; the m. p. of a mixture of the specimens was not depressed.

*6-Hydroxy-2-benzoyloxy-4-benzoyloxybenzaldehyde*.—A solution of *O*-benzoylphloroglucinaldehyde (5.4 g.) and benzyl chloride (7.5 g.) in acetone (40 c.c.) was shaken during 14 hours with silver oxide (7.0 g.). The silver compounds were separated, washed with acetone, and the united solutions evaporated in a vacuum. The residue was dissolved in ether and the solution washed first with aqueous sodium carbonate and then with 5% aqueous potassium hydroxide. The latter fraction was acidified without delay and the precipitated oil, which solidified in the course of a few hours, was taken up in benzene and the dried solution concentrated to 5—6 c.c. Crystals of the

benzylated aldehyde separated, and these were collected (yield, 1.5 g.; m. p. 198°) and recrystallised first from benzene containing ethyl alcohol (m. p. raised to 201–203°) and finally from light petroleum, forming thin, colourless, rhomboidal plates, m. p. 202–203° (Found: C, 72.6; H, 4.4.  $C_{21}H_{16}O_5$  requires C, 72.4; H, 4.6%). The aldehyde is easily soluble in ethyl alcohol, more sparingly soluble in benzene and very sparingly soluble in light petroleum. In alcoholic solution, it gives with ferric chloride a reddish-brown coloration which suggests that the substance is 6-hydroxy-2-benzoyloxy-4-benzyloxybenzaldehyde.

4:6-Diacetoxy-2-methoxybenzaldehyde.—2-O-Methylphloroglucin-aldehyde (Herzig and Wenzel, *Monatsh.*, 1903, 24, 860; Karrer and Glattfelder, *Helv. Chim. Acta*, 1921, 4, 724) was prepared from phloroglucinol monomethyl ether (Herzig and Aigner, *Monatsh.*, 1900, 21, 435) by the Gattermann reaction. In the final stage, it was found advisable to wash the aldimine hydrochloride with fresh ether, to dry it in a vacuum, and to hydrolyse it at 80° with about 10 times its weight of water for 25–30 minutes. The aldehyde crystallised during the process in yellow needles, which were almost pure, m. p. 200–202°, after a single recrystallisation from dilute alcohol. When hydrolysis is effected in the presence of mineral acid, the product is brown (Herzig and Wenzel, *loc. cit.*) and dissolves in aqueous sodium carbonate with a greenish fluorescence which renders it valueless for our purpose.

The aldehyde was only incompletely acetylated by ice-cold aqueous sodium hydroxide (4 mols.) and ethereal acetic anhydride (3 mols.), but readily under the conditions of Pratt and Robinson (J., 1925, 1184). Anhydrous potassium carbonate (2 g.) was added in small amounts to a mixture of acetic anhydride (5 c.c.) and finely powdered 2-O-methylphloroglucinaldehyde (1 g.) so as to maintain a vigorous evolution of carbon dioxide. The pasty mass was kept for 1 hour, water added, and the product stirred with potassium bicarbonate until the excess of acetic anhydride had been decomposed; it was then collected, washed with water, and dried. Recrystallised from benzene–light petroleum, light petroleum, and finally ligroin, the 4:6-diacetoxy-2-methoxybenzaldehyde formed colourless plates, m. p. 107° (Found: C, 56.8; H, 4.6.  $C_{12}H_{12}O_6$  requires C, 57.1; H, 4.8%). This derivative was very easily soluble in alcohol or benzene, more sparingly so in ligroin, light petroleum or ether. An alcoholic solution gave no reaction with ferric chloride, but when an aqueous-alcoholic solution was heated hydrolysis occurred and a reddish-brown ferric chloride reaction was observed.

The substance was also obtained by the methylation of O-diacetylphloroglucinaldehyde (Robertson and Robinson, J., 1927, 1712),

in the preparation of which the following quantities were employed : phloroglucinaldehyde 5 g., acetic anhydride 14 c.c., *N*-sodium hydroxide 100 c.c. The yield was about 6 g., m. p. 102—103°, from 20 g. of phloroglucinaldehyde. *O*-Diacetylphloroglucinaldehyde (1.05 g.) and methyl iodide (2.1 g.) in acetone (5 c.c.) were shaken with silver oxide (1.8 g.) during 6 hours. Isolated in the usual manner, only 0.1—0.2 g. of material, insoluble in sodium hydroxide, was obtained. *O*-Diacetylphloroglucinaldehyde (2.4 g.) and methyl iodide (4.5 g.) in acetone (15 c.c.) were shaken with silver carbonate (6 g.) during 16 hours; evolution of carbon dioxide then appeared to have ceased. The silver compounds were separated and washed with acetone, and the filtrates evaporated in a vacuum. The residue crystallised in contact with ether in colourless elongated plates (0.9 g., m. p. 106—107°). The mother-liquor furnished a small additional amount (0.5 g.) of crystalline material. Recrystallised from ligroin, the main fraction was obtained in colourless elongated plates, m. p. 107—108° alone or mixed with the acetylated 2-methylphloroglucinaldehyde.

*5-O-Benzoyl-7:3':5'-O-trimethyldelphinidin Chloride*.—In the presence of dry hydrogen chloride, a solution of 4-*O*-methylphloroglucinaldehyde in ethyl acetate or ether rapidly becomes brownish-red and deposits a brownish or reddish-brown amorphous substance (xanthylum salt?). For this reason, the benzoylated aldehyde was employed for the condensations to flavylum salts. A solution of 4-*O*-methyl-2-*O*-benzoylphloroglucinaldehyde (1.35 g.) and  $\omega$ -acetoxy-4-benzyloxy-3:5-dimethoxyacetophenone (1.72 g.) (Bradley and Robinson, J., 1928, 1560) in ethyl acetate (30 c.c.) was cooled in ice while being saturated with dry hydrogen chloride, and then kept at room temperature over-night. An intense reddish-purple solution was very rapidly formed, and the flavylum salt crystallised in fine needles, which were collected, washed with ethyl acetate, ether, and dried, forming a green spongy mass (yield, 1.98 g.). An additional amount of equally pure material (0.15 g.) separated from the mother-liquor during 48 hours. The salt was recrystallised by cooling a hot solution in methyl alcohol containing concentrated hydrochloric acid (about 7 vols. %); the fine needles obtained appeared purple by transmitted and lustrous green by reflected light (Found: C, 59.5; H, 4.6; Cl, 6.8.  $C_{25}H_{21}O_8Cl \cdot H_2O$  requires C, 59.8; H, 4.6; Cl, 7.1%).

This salt is practically insoluble in hydrochloric acid; hot 1% hydrochloric acid dissolves it to a pink solution which, when cold, gives with aqueous sodium carbonate only a yellow coloration. The violet-red alcoholic solution is readily decolorised on dilution, and the colour is restored by the addition of acid. A freshly pre-

pared solution of the salt in methyl alcohol gives, with solid sodium acetate, only a lilac coloration. Aqueous sodium carbonate, added to an acidified methyl-alcoholic solution, gives a pale blue coloration, which fades almost completely. Under the same conditions, 5% sodium hydroxide solution gives a bluish-green solution which rapidly becomes pale green and finally yellow. The solution of the salt in concentrated sulphuric acid is violet-red and not fluorescent.

7:3':5'-O-Trimethyldelphinidin Chloride (*Hirsutidin Chloride*) (VI).—Hydrolysis of the benzoyl derivative could not be conveniently effected by aqueous sodium hydroxide, since complete solution was not attained even after several hours. After several trials, the following procedure was adopted. The crude crystalline benzoyl derivative (0.7 g.) was finely powdered and suspended in methyl alcohol (7 c.c.) through which a current of hydrogen was passed. Potassium hydroxide (0.9 g.) in water (3 c.c.) was then added. Dissolution was effected in 10–15 minutes, and the blue solution initially produced changed slowly through green to deep orange. After 4 hours, concentrated hydrochloric acid (3.4 c.c.) was added, and this precipitated a voluminous colourless solid which filled the liquid. Gently warmed at 50–60° during 25–30 minutes, this dissolved to a clear, deep red solution, from which the debenzoylated flavylum salt separated during the process in a well-crystallised condition (yield, 0.26 g.), leaving the mother-liquor almost colourless.

This crude product was dried, washed with ether, and a portion (0.4 g.) added to boiling methyl alcohol (60 c.c.). After 4–5 minutes, the solution was filtered (undissolved residue, 0.06 g.) and concentrated hydrochloric acid (2 c.c.) was added to the filtrate, which was kept at 50–55° while concentrated hydrochloric acid (8 c.c.) was added in portions of 1 c.c.: each addition was accompanied by the precipitation of a quantity of the flavylum salt. After 12 hours, the crystals were collected and dried in air (yield, 0.15 g.). The salt was obtained in short, dark red, pointed prisms, which were frequently arranged in rosettes (Found: C, 56.5; H, 4.6; Cl, 9.1.  $C_{18}H_{17}O_7Cl$  requires C, 56.8; H, 4.5; Cl, 9.3%).

Heated with water, the salt dissolves to a weak red solution with a slight violet tinge, but this fades rapidly at the boiling point and becomes colourless; the red colour is restored by the addition of acid. In hot 0.5% hydrochloric acid, the salt is already sparingly soluble; it dissolves to a reddish solution, whereas a cold saturated solution in 4% hydrochloric acid is only pink. The cooled solution in hot 0.25% hydrochloric acid presumably contains much pseudo-base, since excess of aqueous sodium carbonate gives a brownish-green solution which changes to olive-green. The fresh dilute

solution in methyl alcohol is violet-red and gives with sodium carbonate solution or solid sodium acetate a pure blue coloration. On the other hand, when the solution is kept for some time previous to the test, a greenish-blue coloration is obtained. The salt dissolves in aqueous *N*/10-sodium hydroxide to a purple-blue solution which rapidly becomes crimson-blue (dichroic) and then fades to emerald-green.

*5:3':5'-O-Trimethyladelphinidin Chloride* (V).—2-*O*-Methylphloroglucinaldehyde resembles its isomeride in yielding in ethereal ethyl acetate or formic acid solution, in the presence of dry hydrogen chloride, an amorphous brownish-red substance, which is soluble in water and alcohol but insoluble in ether or benzene and dissolves in aqueous alkalis to red solutions exhibiting green fluorescence.

In many of our preliminary experiments on the aldehyde-ketone condensations, a fluorescent by-product was obtained, and the intensity of the fluorescence was apparently greater than that resulting by self-condensation of the aldehyde alone. The proportion of this by-product appeared to be smaller in formic acid than in ethyl acetate solution, and it was completely eliminated by the following procedure.

A solution of  $\omega$ -acetoxy-4-benzyloxy-3:5-dimethoxyacetophenone (2.0 g.) in formic acid (10 c.c.) was saturated with dry hydrogen chloride at room temperature, and 2-*O*-methylphloroglucinaldehyde (0.8 g.) was then added in several small portions during 5 hours. A deep crimson solution was rapidly formed (in previous experiments the medium became brownish-red) and a well-crystallised substance separated. After 12 hours this was collected, washed with formic acid and then with ethyl alcohol (8 c.c.) containing concentrated hydrochloric acid (2 c.c.), and dried in the air (0.35 g.). An additional amount of material separated during 2 days, but the solution was too viscous to permit of filtration and the salt was more conveniently isolated by diluting the product with alcohol (50 c.c.) containing concentrated hydrochloric acid (20 c.c.) and collecting the precipitate which slowly formed. This fraction was not completely crystalline (yield, 0.9 g.).

The crystalline material was recrystallised by solution in methyl alcohol containing 2.5% by volume of concentrated hydrochloric acid and addition of concentrated hydrochloric acid to the filtered solution (Found: C, 56.1; H, 4.5; Cl, 9.1%). This specimen was recrystallised by dissolving 0.1 g. of the salt in methyl alcohol (350 c.c.) containing concentrated hydrochloric acid (9 c.c.), and adding concentrated hydrochloric acid (40 c.c.) to the filtered solution. Collected and dried in air, this material was a green crystalline powder having a bright yellow lustre (Found: C, 56.1; H, 4.5;

Cl, 9.2.  $C_{18}H_{17}O_7Cl \cdot 0.25H_2O$  requires C, 56.1; H, 4.5; Cl, 9.2%). It was seen under the microscope to consist of dark red, hexagonal tables and short slender prisms, and it may have contained two hydrates, as the analyses suggested, one having been precipitated immediately on the addition of acid to the warm solution and the other having crystallised more slowly on cooling. The salt dissolves in sodium carbonate solution with a pure blue colour, and the same colour is obtained by adding sodium acetate to a freshly prepared solution in methyl alcohol.

To test the possibility of the presence of benzylated material, a portion of the specimen first analysed (0.1 g.) was finely powdered, suspended in glacial acetic acid (100 c.c.), and heated at  $80^\circ$  in a stream of dry hydrogen chloride during 3 hours. Only a very small portion of the salt dissolved, but complete debenzylation was assured under these conditions. The product was collected, washed, and dried: it gave the same qualitative reactions as the original specimen.

*Comparison of the Colour Reactions of Hirsutidin Chloride (H) with those of 7 : 3' : 5'-O-Trimethyldephinidin Chloride (S) and of 5 : 3' : 5'-O-Trimethyldephinidin Chloride (A).*—All the reactions of H were found on direct comparison to be identical with those of S and to differ from those of A. When ammonia was added to an alcoholic solution, a greenish-blue solution resulted; when derived from H or S, this was blood-red by transmitted artificial light, but under these conditions the A solution was violet or bluish-violet. By transmitted sunlight, H and S solutions were blue and violet in thick layers; A was greenish-blue. Alcoholic solutions of H and S were magenta; that of A was violet.

Under the standard procedure of Robertson and Robinson (*loc. cit.*), the colours in a range of buffered solutions from  $p_H$  3.2 to  $p_H$  11.6 were the following:—

H and S: (1) bluish-red, rapidly changing to brownish-red; (2) the same; (3) reddish-brown; (4) weak brownish-red; (5) violet tinged brownish-red; (6) fading violet; (7) bluish-violet, blue in thin layers; (8)—(15) inclusive, blue, red in shade by comparison with (A) solutions.

After  $\frac{1}{2}$  hour: (1), (2), (3) and (4), almost colourless but more coloured than (A) solutions; (5) very weak brownish-red; (6), (7) and (8), increasing violet; (9)—(12), blue, violet by transmitted artificial light; (13), (14) and (15), blue, redder violet by transmitted artificial light.

After 24 hours: (1)—(5), colourless; (6)—(8), increasing pale violet; (9)—(12), bluish-green; (13)—(15), greenish-blue.

(A) gave colours in marked contrast, on direct comparison: (1)



bluish-red; (2) same; (3) same, but fading; (4) bluer red, fading quickly; (5) reddish-violet, fading; (6) violet, fading; (7) and (8) no change; (9)—(15) inclusive, blue with green shade.

After  $\frac{1}{2}$  hour: (1)—(8), almost colourless; (9) very pale violet-blue; (10) blue, very different from (9); (11)—(15), greenish-blue.

After 24 hours: (1) and (2), colourless; (3), (4) and (5), colourless, minute flocculent precipitate (none in H and S); (6), (7), (8) and (9), very feeble yellowish-green; (11) and (12), very pale greenish-yellow; (13) weak orange-yellow; (14) and (15), pale orange.

Throughout, blue solutions of H and S were much redder by artificial light, but A gave blue solutions even when examined by artificial light.

4:5-*Dihydroxy-3-methoxybenzaldehyde* (XI).—A mixture of 5-bromovanillin (31 g.), copper bronze (12 g.), and 8% sodium hydroxide solution (600 c.c.) was heated in a rotating autoclave at 200—210° during 1 hour. The cooled product was acidified with a slight excess of dilute sulphuric acid and filtered from a small tarry precipitate; after 12 hours, crystalline material (0.98 g.) had separated and this also was removed. The dark filtrate (1400 c.c.) was concentrated under diminished pressure. The distillate (800 c.c.) gave only 0.24 g. of a red insoluble precipitate when mixed with an excess of 2:4-dinitrophenylhydrazine hydrochloride in 2*N*-hydrochloric acid. The residual solution was extracted with ether and the dark product so isolated was extracted with benzene, yielding almost pure 3-*O*-methylgallaldehyde (19.4 g.), m. p. 129—131° with slight previous softening. The aldehyde crystallised from water, benzene or light petroleum in almost colourless needles, m. p. 132—134° (Found in material dried at 100° in a vacuum: C, 57.3; H, 4.8.  $C_8H_8O_4$  requires C, 57.1; H, 4.8%).

The 2:4-dinitrophenylhydrazone was precipitated when a cold solution of the aldehyde (0.44 g.) in water was added to an excess of 2:4-dinitrophenylhydrazine in 2*N*-hydrochloric acid. The solid was collected and dried at 100° (yield, 0.83 g. Calc., 0.88 g.). The hydrazone crystallised from ethyl alcohol, in which it was sparingly soluble, in dark red, pointed prisms, which began to decompose at 230° (Found in material dried over sulphuric acid: C, 48.2; H, 3.7; N, 15.5, 15.9.  $C_{14}H_{12}O_7N_4$  requires C, 48.3; H, 3.5; N, 16.1%).

*Methylation.* Methyl sulphate (2.5 g.) and aqueous sodium hydroxide (10 c.c. of 10%) were added gradually and alternately to a suspension of the aldehyde (0.5 g.) in water (5 c.c.). The whole was mechanically shaken during 1 hour and then sodium hydroxide solution (10 c.c. of 20%) was added and the shaking continued.

During this process, the methylated aldehyde separated from the strongly alkaline solution in colourless needles (0.33 g.), m. p. 73—75°, and, after recrystallisation, m. p. 74—75° (Heffter and Capellmann give m. p. 77°, and Semmler and Mauthner, respectively, record the m. p.'s 75° and 74—75° for 3:4:5-trimethoxybenzaldehyde).

*Acetylation.* The aldehyde (1.7 g.) was acetylated by dissolving it in ether containing acetic anhydride (6 g.) and shaking the solution with water to which 5% aqueous potassium hydroxide (68 c.c.) was added in small successive amounts, the whole being cooled to 0°. The separated ethereal solution was washed with 5% aqueous potassium hydroxide, then with dilute sulphuric acid and water. The product crystallised from benzene—light petroleum in needles, m. p. 98—99° (Shriner and McCutchan record the m. p. 102—103° for the acetylation product, prepared by another method, and, on analysis, obtained data in agreement with the formula  $C_{12}H_{12}O_7$ , which indicates that the substance crystallises with  $1H_2O$ ).

*Methyl 5-Hydroxy-3:4-diphenylmethylenedioxybenzoate* (VIII).—In the course of preliminary experiments on the condensation of diphenyldichloromethane with methyl gallate, considerable quantities of a sparingly soluble, oily by-product, probably  $CPh_2[O \cdot C_6H_2(OH)_2 \cdot CO_2Me]_2$ , were obtained. A two-stage process under the following conditions gave the best results.

A solution of methyl gallate (84 g.) and pyridine (36.5 c.c.) in acetone (200 c.c.) was added to one of diphenyldichloromethane (108 g.) in acetone (100 c.c.) and kept for 12 hours. A solution of sodium hydroxide (37 g.) in water (100 c.c.) was then slowly added; the temperature rose and reached the boiling point of the mixture; after 2 hours, the whole was added to water (2000 c.c.). The brown oily material was separated and dissolved in ether, and the extract washed with aqueous sodium carbonate and then with aqueous sodium hydroxide (20 g. in 400 c.c.). The *methyl* ester precipitated from the latter extract on acidification was collected; it crystallised from benzene (yield, 60 g.; m. p. 163° after two crystallisations) in colourless needles, m. p. 165° (Found: C, 73.6; H, 5.0; loss at 110° in a vacuum, 10.1.  $C_{21}H_{16}O_5 \cdot 0.5C_6H_6$  requires C, 73.7; H, 5.1;  $C_6H_6$ , 10.1%).

The presence of benzene in this material was confirmed by means of a test devised by Professor W. Ramsden. This can be used for the detection of traces of aromatic hydrocarbons, and depends on the insoluble film (often pink) obtained by condensation with formaldehyde in the presence of concentrated sulphuric acid. It may be demonstrated by shaking one drop of benzene with half a test-tube full of water, pouring away the liquid, and adding a few

c.c. of sulphuric acid and two or three drops of 40% aqueous formaldehyde.

*Methyl 3-Methoxy-4:5-diphenylmethylenedioxybenzoate* (Methyl ester of IX).—Methyl hydroxydiphenylmethylenedioxybenzoate (68 g.) was dissolved in hot methyl alcohol (300 c.c.), the solution cooled and forthwith mixed with an alcoholic solution of sodium ethoxide (4.5 g. of sodium in 50 c.c.) and methyl iodide (20 c.c.). The mixture was gently boiled for  $\frac{1}{2}$  hour and, on cooling, short colourless prisms (61 g.), m. p.  $134.5^\circ$ , separated; the m. p. was not raised by recrystallisation (Found: C, 72.8; H, 5.2.  $C_{22}H_{18}O_5$  requires C, 72.9; H, 5.0%). The ester (20 g.) was refluxed for 2 hours with water (100 c.c.) and potassium hydroxide (6 g.); the precipitate obtained on acidification of the cooled solution crystallised from aqueous acetone in thick polyhedral plates (16 g.), m. p.  $217^\circ$  (Found: C, 72.3; H, 4.7.  $C_{21}H_{16}O_5$  requires C, 72.4; H, 4.6%).

This *3-methoxy-4:5-diphenylmethylenedioxybenzoic acid* (8 g.) was mixed with carbon tetrachloride (12 c.c.) and phosphorus pentachloride (8 g.), and the whole gently boiled until the evolution of hydrogen chloride slackened. The chloride crystallised, on the addition of light petroleum to the cooled clear liquid, in large compact prisms (1.5 g.), m. p.  $109^\circ$  (Found: Cl, 9.9.  $C_{21}H_{15}O_4Cl$  requires Cl, 9.7%).

*$\omega$ -Diazo-3-methoxy-4:5-diphenylmethylenedioxyacetophenone*,  $C_{22}H_{16}O_4(C_6H_5)_2(OMe)CO \cdot CHN_2$ .—A solution of methoxydiphenylmethylenedioxybenzoyl chloride (8.5 g.) in chloroform (20 c.c.) was slowly added to an ethereal solution of diazomethane (from 13 c.c. of nitrosomethylurethane and 75 c.c. of ether) cooled in a freezing mixture. A brisk evolution of nitrogen occurred and pale yellow needles separated (7.5 g.). The substance crystallised from benzene-light petroleum in yellow needles, which became darker at  $135^\circ$  and decomposed from  $160$ – $170^\circ$ : these temperatures, however, are not characteristic and depend on a particular rate of heating (Found: C, 70.7; H, 4.6; N, 7.2.  $C_{22}H_{16}O_4N_2$  requires C, 70.9; H, 4.4; N, 7.5%).

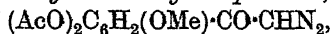
*$\omega$ -Acetoxy-3-methoxy-4:5-diphenylmethylenedioxyacetophenone* (XII).—The foregoing diazo-ketone (7.5 g.) was cautiously heated with acetic acid (20 c.c.) on the steam-bath for 15 minutes; the acetic acid was then distilled in a good vacuum. The residue crystallised from benzene-light petroleum in stout prisms (6.3 g.), m. p.  $126$ – $127^\circ$  (Found: C, 71.6; H, 5.2.  $C_{24}H_{20}O_6$  requires C, 71.3; H, 5.0%).

*3-O-Methylgallic Acid* (X).—A mixture of methyl 3-methoxy-4:5-diphenylmethylenedioxybenzoate (40 g.) and concentrated hydrochloric acid (150 c.c.) was refluxed for 2 hours, cooled, and neutralised with potassium bicarbonate. The undissolved benzo-

phenone was pulverised, and the filtered solution acidified with hydrochloric acid, giving 16 g. of grey needles. The acid crystallised from water (charcoal) in elongated colourless prisms, m. p. 220°, in agreement with Fischer's statement (*loc. cit.*). The air-dried product was found to contain  $\frac{1}{2}\text{H}_2\text{O}$  (Found: C, 49.6; H, 4.8; loss at 110° in a vacuum, 4.8. Calc. for  $\text{C}_8\text{H}_8\text{O}_5 \cdot \frac{1}{2}\text{H}_2\text{O}$ : C, 49.7; H, 4.7;  $\text{H}_2\text{O}$ , 4.7%). The *diacetyl* derivative was obtained by heating the acid (16 g.) with acetic anhydride (60 g.) and zinc chloride (1.5 g.) on the steam-bath for 2 hours. The product was purified by solution in aqueous potassium bicarbonate and recovery; it finally crystallised from aqueous alcohol in colourless prisms (17 g.), m. p. 170–171° (Found: C, 53.8; H, 4.7.  $\text{C}_{12}\text{H}_{12}\text{O}_7$  requires C, 53.7; H, 4.5%).

4 : 5-Diacetoxy-3-methoxybenzoyl chloride was obtained by heating a mixture of the acid (15 g.), phosphorus pentachloride (12 g.), and chloroform (17 c.c.) until solution occurred and the reaction was completed. On addition of light petroleum and cooling in a freezing mixture, the derivative separated; it crystallised from carbon tetrachloride in stout prisms, m. p. 109° (Found: Cl, 12.6.  $\text{C}_{12}\text{H}_{11}\text{O}_6\text{Cl}$  requires Cl, 12.4%).

$\omega$ -Diazo-4 : 5-diacetoxy-3-methoxyacetophenone,



was obtained by the usual method and precipitated from the reaction mixture on the addition of light petroleum as a quickly crystallising oil (7 g. from 9.5 g. of the chloride). It crystallised from benzene–light petroleum at a low temperature in pale yellow, short prisms, m. p. 90–91° (Found: C, 53.4; H, 4.4; N, 9.2.  $\text{C}_{13}\text{H}_{12}\text{O}_6\text{N}_2$  requires C, 53.4; H, 4.1; N, 9.6%).

$\omega$  : 4 : 5-Triacetoxy-3-methoxyacetophenone (XIII).—The foregoing diazo-ketone (5 g.) gave in the usual way 4.8 g. of pale yellow prisms. The substance crystallised from benzene–light petroleum in elongated prisms, m. p. 138.5°, softening at 136° (Found: C, 55.4; H, 5.0.  $\text{C}_{15}\text{H}_{16}\text{O}_8$  requires C, 55.5; H, 5.0%).

5-O-Benzoyl-3'-O-methylidelpinidin Chloride (XIV).—(A) This is much the better of the two methods for the preparation of the salt; the condensation occurs with greater facility and the yield is higher than in (B).

A solution of  $\omega$ -acetoxy-3-methoxy-4 : 5-diphenylmethylenedioxyacetophenone (1.6 g.) and 2-O-benzoylphloroglucinaldehyde (1 g.) in ethyl acetate (60 c.c.) was cooled in melting ice, saturated with hydrogen chloride, and kept for 12 hours under the pressure of the hydrogen chloride generator. The dark violet deposit of prisms, brown by transmitted light under the microscope, was collected (1 g.) and crystallised (0.9 g.) by solution in hot ethyl

alcohol (200 c.c.) containing a few drops of concentrated hydrochloric acid and addition of 7% hydrochloric acid (200 c.c.) to the filtered solution. The glistening needles (0.5 g.) that separated had a fine bronze lustre (Found: C, 55.9; H, 4.4; MeO, 6.0; Cl, 7.1.  $C_{23}H_{17}O_8Cl \cdot 2H_2O$  requires C, 56.1; H, 4.3; 1MeO, 6.3; Cl, 7.2%).

The substance is insoluble in water and acetone and very sparingly soluble in hot dilute hydrochloric acid. It gives a crimson alcoholic solution, becoming blue on the addition of ferric chloride. The alkali-colour reactions resemble those of *O*-benzoylcyanidin and *O*-benzoyldelphinidin chlorides.

(B) A mixture of  $\omega$ :4:5-triacetoxy-3-methoxyacetophenone (1.2 g.), 2-*O*-benzoylphloroglucinaldehyde (1 g.), and alcohol (25 c.c.) was cooled in melting ice and saturated with hydrogen chloride whilst being vigorously mechanically stirred. The temperature was then maintained at 35° for 2 hours, after which the dark red, homogeneous liquid was cooled in ice, and acetyl chloride (25 c.c.) slowly added during 1 hour. Next day, the violet deposit was collected (0.5 g.) and crystallised as described under (A). The colour reactions and other properties of this specimen were identical with those of the product obtained by the method A. It was apparent that the presence of the acetoxy-groups attached to the aromatic nucleus retarded the condensation, and flavylium salt was only obtained under conditions favouring the removal of the acetyl residues by hydrolysis. Herein lies the explanation of the necessity for the period of heating at 35° and the selection of a hydroxylic solvent.

3'-*O*-Methyldelphinidin Chloride (XV).—The benzoyl derivative (0.5 g.) was added to alcohol (5 c.c.) and 10% aqueous sodium hydroxide (5 c.c.), and the mixture kept for 2 hours and occasionally shaken; air was excluded by hydrogen, washed by permanganate and alkaline pyrogallol. After the addition of concentrated hydrochloric acid (3 c.c.), the whole was heated on the steam-bath for 1 hour, cooled, and more hydrochloric acid (10 c.c.) added. The dark precipitate was washed with acetone and ether and dried. The crude product was dissolved in ethyl alcohol (125 c.c.), containing a few drops of concentrated hydrochloric acid, and the filtered solution mixed with an equal volume of 7% hydrochloric acid. The chloride crystallised in yellowish-green, elongated, rhombohedral plates, yellowish-brown by transmitted light under the microscope (Found: C, 51.6; H, 4.0; Cl, 9.6; loss at 110° in a vacuum, 3.4. Found in material dried at 110°: C, 53.4; H, 3.9; Cl, 9.8.  $C_{16}H_{13}O_7Cl \cdot H_2O$  requires C, 51.9; H, 4.1; Cl, 9.6;  $\frac{1}{2}H_2O$ , 2.4%.  $C_{16}H_{13}O_7Cl \cdot \frac{1}{2}H_2O$  requires C, 53.2; H, 3.9; Cl, 9.8%). Apparently the salt loses rather more than  $\frac{1}{2}H_2O$  at 110°, but, being then very

hygroscopic, regains the composition  $C_{16}H_{13}O_7Cl \cdot \frac{1}{2}H_2O$  during the brief period of exposure preceding the analysis of the dried material by combustion.

*3'-O-Methyldelphinidin chloride* closely resembles cyanidin chloride in its general properties; the alcoholic acid solutions are a little bluer, and the precipitation of colour-base on the addition of water, so characteristic of cyanidin, does not take place to the same extent. The colour reactions in a range of buffered solutions (Robertson and Robinson, *loc. cit.*) were the following :—

(1) Deep cherry-red; (2) very slightly bluer; (3) the same; (4) a little bluer; (5) a little bluer, still cherry-red; (6) reddish-violet; (7) bluer reddish-violet; (8) bluer violet; (9) violet-blue in thin layers; (10) blue; (11), (12) and (13), greener blue; (14) greenish-blue, fading very rapidly; (15) greenish-blue, quickly changing to pale green. (3), (4) and (5) faded rapidly to brownish-red, and the presence of colour-base was confirmed by centrifuging the solution in a high-speed apparatus, a solid deposit and a colourless solution then being obtained.

After  $3\frac{1}{2}$  hours, the colours were: (1) and (2), colourless; (3), (4) and (5), colourless, brownish-red precipitate; (6) reddish-violet, a little precipitate; (7), (8) and (9), violet; (10), (11), (12) and (13), a series from greenish-blue to bluish-green; (14) and (15), orange.

After 24 hours: (1)—(8), colourless, with precipitate in (4), (5) and (6); (9)—(13), very weak orange to weak orange; (14) and (15), a little deeper orange.

These appearances (denoted as caused by S) were directly compared with those produced under the same conditions by natural petunidin chloride (P) (Willstätter and Burdick, *loc. cit.*), natural myrtilidin chloride (M) (Willstätter and Zollinger, *Annalen*, 1915, 408, 83; 1916, 412, 205), for specimens of which we are deeply indebted to Professor R. Willstätter, and with mixtures (DM) of malvidin chloride and delphinidin chloride. There was a very close resemblance between all these series when the anthocyanidin and buffered solutions were first mixed, especially between S and P, the only divergence being that P did not separate colour-base in (3), (4) and (5). S and P remained similar and, after 24 hours, were identical, but S and M diverged at several points after 10 minutes, and this divergence reached a maximum after 1 hour; after 24 hours, there were still marked differences, but, on long keeping, both S and M exhibited the deepest orange colour at (9) and (10). DM gave colours undoubtedly closer to M than to P, but there were differences between M and DM at certain points. Colorimetric observations of the blue ferric chloride and copper sulphate reactions in alcoholic solution showed that the order (stronger to

weaker) was : S, P, M, DM; the ratio of intensity S/P was about 7/5.

The only conclusion which can be legitimately drawn from these observations at the present stage is that petunidin is not perfectly pure 3'-O-methyldelphinidin, but it is still possible that the anthocyanidin has essentially this constitution. Small percentages of impurities would suffice to change the crystal form and alter the composition of the hydrate.

Further work on this unsolved problem is in progress.

The authors wish to thank the Swiss Commission of the Ramsay Memorial Fellowships Trust for a fellowship awarded to one of them.

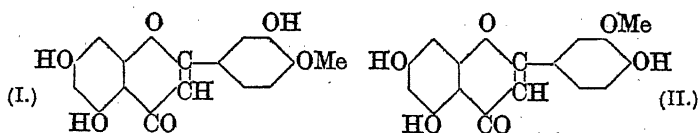
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### CVIII.—*Anthoxanthins. Part XI. A Synthesis of Diosmetin and of Luteolin 3'-Methyl Ether.*

By ALBERT LOVECY, ROBERT ROBINSON, and SHIGEHICO SUGASAWA.

THE rhamnoglucoside, diosmin, was isolated in 1925 by Oesterle and Wander (*Helv. Chim. Acta*, 8, 519) from *Scrophularia nodosa*, *Hyssopus officinalis*, as well as from species of *Conium*, *Barosma*, *Hedeoma*, *Menika*, *Toddalia*, and *Linaria*, and found to yield an aglycone, diosmetin (I), which was shown to be a methyl ether of luteolin. The isovanillin-type of orientation is so infrequently



encountered in nature that it was thought desirable to synthesise diosmetin and the isomeride (II) which, according to A. G. Perkin (J., 1900, 77, 423), stands in a close relationship to scoparin from *Cytisus scoparius* (Link).

The two flavones have been obtained by debenzoylation of the benzyl ethers produced by condensation of phloracetophenone with sodium *O*-benzylisovanillate and *O*-benzylvanillate, respectively. The methods employed are thus quite parallel with that devised for the synthesis of syringetin (Heap and Robinson, Part IX, J., 1929, 67). The synthetic diosmetin and its triacetate were directly compared with specimens of the natural product and of its triacetate

kindly sent to us by Professor O. A. Oesterle, to whom we are deeply indebted, and no divergences of behaviour were observed.

#### EXPERIMENTAL.

*isoVanillic Acid*.—This substance can be obtained by the hydrolysis of veratric acid by means of acids, the methoxyl group in the *m*-position to the carboxyl being preferentially attacked (compare 4-nitroveratrole; Cardwell and Robinson, J., 1915, 107, 255).

A mixture of veratric acid (20 g.) and hydrobromic acid (200 c.c. of 40%) was boiled under reflux; after 1–1½ hours, a clear yellowish-brown solution was obtained, but in a short time a white substance was deposited; when the voluminous precipitate had become crystalline, it was collected on a sintered-glass filter-plate. The crude material (8–9 g.), m. p. 245–247° after sintering at 235°, was pure enough for many purposes; once crystallised from water, it had m. p. 248–249° (literature, 250°). The hot acid filtrate deposited a white flocculent material on cooling and, by renewed treatment with boiling 40% hydrobromic acid, a further quantity of *isovanillic acid* (about 1 g.) was obtained (total yield, 50–55%).

*O-Benzylisovanillic Acid and Derivatives*.—The direct benzylation of *isovanillic acid* gave indifferent results, owing to separation difficulties, and accordingly we adopted the following processes :

(A) Following Shinoda (*J. Pharm. Soc. Japan*, 1928, 48, 936), we prepared *isovanillin* (25 g., m. p. 115°) by the semi-demethylation of veratraldehyde (100 g.) by means of boiling 43% hydrobromic acid (1500 g.) during 3 hours. The dark filtrate from tarry matter was extracted with chloroform, and the residue after removal of the solvent was dissolved in aqueous potassium hydroxide and freed from neutral substances by extraction with ether. The hydroxy-aldehyde was regenerated, isolated by means of chloroform, and crystallised from water (600 c.c.).

*isoVanillin* (90 g.), dissolved in a solution of potassium hydroxide (34 g.) in water (200 c.c.), was mixed with benzyl chloride (50 g.), and the whole heated (oil-bath at 110–120°) for 7 hours with frequent shaking. The product was isolated by extraction with chloroform and crystallisation from alcohol (yield, 80 g.; recrystallised, 66 g., m. p. 62–63°) in colourless needles, m. p. 63° (Found : C, 74.4; H, 5.8.  $C_{15}H_{14}O_3$  requires C, 74.5; H, 5.8%). Mixed with benzylvanillin (m. p. 63°), it melted at about 48°. Oxidation of *O-benzylisovanillin* was effected by means of potassium permanganate in acetone solution, the best results being obtained in relatively small-scale operations (less than 15 g.). The acid crystallised from alcohol and then from ethyl acetate in white, elongated, hexagonal plates, m. p. 177–178°.



(B) This is the better of the alternatives. *iso*Vanillic acid gave an equal weight of the methyl ester (crystallised from ether-light petroleum; m. p. 65–66°) on treatment in the usual way with methyl alcohol and hydrogen chloride.

Potassium hydroxide (5.5 g.) in methyl alcohol (50 c.c.) was added to a mixture of methyl *isovanillate* (17 g.), benzyl chloride (12 g.), and methyl alcohol (25 c.c.), and the whole heated on the steam-bath for 5 hours. Potassium chloride and methyl *O-benzylisovanillate* separated from the hot solution and, after cooling, the ester was collected and washed with water (yield, 21.5 g. or 82%; m. p. 121°); recrystallised from methyl alcohol-acetone, it melted at 124° (Found: C, 70.8; H, 6.1.  $C_{16}H_{14}O_4$  requires C, 70.6; H, 5.9%). A mixture of methyl *O-benzylisovanillate* (52 g.), potassium hydroxide (12 g.), and water (120 c.c.) was heated on the steam-bath for 2 hours, and the clear solution then acidified. *O-Benzylisovanillic acid*, crystallised from acetic acid, had m. p. 177° (Found: C, 69.4; H, 5.6.  $C_{15}H_{14}O_4$  requires C, 69.8; H, 5.4%).

*O-Benzylisovanillic Anhydride*.—A cold ethereal solution of pure thionyl chloride (3.7 g.) was added during 2 hours with stirring to a suspension of powdered benzylisovanillic acid (12.5 g.) in dry ether (50 c.c.) and pyridine (5.3 g.) cooled in a mixture of ice and salt. The whole was kept at 0° for several hours with occasional shaking, crushed ice was then added, and the solid was collected and triturated successively with ice-cold dilute hydrochloric acid, dilute aqueous sodium carbonate, and water, and dried in a vacuum (yield, 11 g.; a small further quantity was recovered by means of ether). The *anhydride* crystallised from benzene or ethyl acetate in glistening needles, m. p. 156° after softening at 153° (Found: C, 72.3; H, 5.3.  $C_{30}H_{26}O_7$  requires C, 72.3; H, 5.2%).

5 : 7 - *Dihydroxy* - 3' - *benzyloxy* - 4' - *methoxyflavone* (*O-Benzylidismetin*).—An intimate mixture of phloracetophenone (5 g.), *O-benzylisovanillic anhydride* (60 g.), and sodium *O-benzylisovanillate* (12 g.) was heated (oil-bath at 190–195°) for 6 hours, and the viscous reddish-brown mass was then poured as completely as possible into alcohol (200 c.c.). The residue in the flask was chipped out when cold and washed out with alcohol and the whole was refluxed for 2 hours. A solution of potassium hydroxide (25 g.) in water (30 g.) was added and the mixture was boiled gently for 30 minutes and then evaporated under diminished pressure. The residue was dissolved in water and saturated with carbon dioxide, giving a yellowish-brown flocculent precipitate, which was redissolved in 2% sodium hydroxide solution and reprecipitated by carbon dioxide (dry wt., 15 g.). Attempts to crystallise this material were unsuccessful, but after treatment with boiling alcoholic potassium

hydroxide about 2 g. of a yellow substance remained undissolved; this was dissolved in 2% sodium hydroxide solution, and the flavone regenerated by means of carbon dioxide. The product now crystallised from acetic acid in pale yellow clusters of needles, m. p.  $240^{\circ}$  after sintering at  $237^{\circ}$  (Found: C, 70.6; H, 4.7.  $C_{23}H_{18}O_6$  requires C, 70.8; H, 4.6%). The alcoholic potassium hydroxide filtrate was also worked up and, by taking advantage of the insolubility of the impurities in alcohol, a further equal quantity of *benzyldiosmetin*, m. p.  $237^{\circ}$ , was recovered.

*O-Triacetyldiosmetin*.—A solution of *O*-benzyldiosmetin (0.4 g.) in acetic acid (25 c.c.) was boiled and transferred to the steam-bath; a solution of hydrochloric acid (2 g.) saturated at  $0^{\circ}$  was then gradually introduced, giving a deep yellow solution. After 10 minutes, a further amount (1 g.) of the acid was added, the heating continued for 30 minutes, and the mixture was finally boiled. Water (30 c.c.) was added to the filtered solution and the pasty precipitate was collected and dried; it could not, however, be crystallised at this stage.

The crude product (0.3 g.) was boiled with acetic anhydride (10 c.c.) and a drop of pyridine for 2 hours and the acetate produced was crystallised from alcohol and then from ethyl acetate, giving colourless needles, m. p.  $195-196^{\circ}$  (Found: C, 72.3; H, 5.3. Calc. for  $C_{22}H_{18}O_9$ : C, 72.3; H, 5.2%). This specimen was identical in every way with specimens of triacetyldiosmetin from two sources, kindly supplied by Professor Oesterle. A mixture of the natural and the synthetic specimen gave an undepressed melting point.

*Diosmetin* (I).—A mixture of the synthetic triacetyldiosmetin (0.3 g.) with alcohol (5 c.c.) and 2% potassium hydroxide solution (10 c.c.) was heated on the steam-bath for 15 minutes, and the flavone isolated from the clear yellow solution by acidification with acetic acid. The substance, crystallised from alcohol and then twice from alcohol-ethyl acetate, formed yellow needles, sintering at  $248^{\circ}$  and melting at  $253-254^{\circ}$  (Found in a specimen dried at  $150^{\circ}$  in a high vacuum: C, 64.3; H, 4.2. Calc. for  $C_{16}H_{12}O_6$ : C, 64.0; H, 4.0%). A mixture with natural diosmetin (sintering at  $245^{\circ}$  and melting at  $253-255^{\circ}$ ) sintered at  $245^{\circ}$  and melted at  $253-254^{\circ}$ . In all respects, the two specimens had identical properties.

*Benzylvanillic Anhydride*,  $[CH_2Ph \cdot O \cdot C_6H_3(OMe) \cdot CO]_2O$ .—The benzylation of vanillin (276 g.) was effected in aqueous solution (compare Gomberg and Buchler, *J. Amer. Chem. Soc.*, 1920, 42, 2059) by means of benzyl chloride (150 g.) and potassium hydroxide, the reaction mixture being heated (oil-bath at  $110-120^{\circ}$ ) for  $10\frac{1}{2}$  hours. After crystallisation, 165 g., m. p.  $63-64^{\circ}$ , were obtained.

On oxidation with potassium permanganate in acetone solution, the aldehyde (70 g.) furnished crystalline *O*-benzylvanillic acid (60 g.), m. p. 168—169°.

*O*-Benzylvanillic acid (97 g.) was finely ground, suspended in dry ether (375 c.c.) and pyridine (40 g.), to which thionyl chloride (28 g.) in ether (30 c.c.) was added, and the whole kept at 0° for 12 hours. Crushed ice was then introduced and the solid was washed successively with ice-cold 2*N*-hydrochloric acid, water, 2*N*-sodium carbonate, and water and dried (80 g., m. p. 135°; benzylvanillic acid, 9 g., was recovered from the ether and washings). The *anhydride* crystallised from ethyl acetate in slender lustrous needles, m. p. 135—136° (Found: C, 72.2; H, 5.4.  $C_{30}H_{26}O_7$  requires C, 72.3; H, 5.2%).

5 : 7-*Dihydroxy-4'-benzyloxy-3'-methoxyflavone*.—An intimate mixture of phloracetophenone (4.5 g.), sodium *O*-benzylvanillate (12 g.), and *O*-benzylvanillic anhydride (40 g.) was heated (oil-bath at 180—185°) for 3 hours subsequent to fusion to a mobile, dark red liquid. The product was refluxed with alcohol (175 c.c.); a solution of potassium hydroxide (17 g.) in water (20 c.c.) was gradually added, and the boiling continued for 30 minutes. The solution was distilled (170 c.c. collected) and the residue was dissolved in water (200 c.c.), heated to 60°, and saturated with carbon dioxide. The buff precipitate was collected (7 g.), redissolved in aqueous potassium hydroxide, and reprecipitated by carbon dioxide (yield, 5 g.). The crude flavone was then acetylated by gently refluxing it with acetic anhydride (20 c.c.) and a drop of pyridine for 2 hours. The acetyl derivative, which separated on cooling (2 g.), crystallised from ethyl acetate in slender white needles, m. p. 195° (1.6 g.) (Found: C, 68.2; H, 4.8.  $C_{27}H_{22}O_8$  requires C, 68.4; H, 4.6%).

This 5 : 7-*diacetoxy-4'-benzyloxy-3'-methoxyflavone* (1.2 g.) was hydrolysed by means of alcoholic potassium hydroxide on the steam-bath and, when the diluted solution was acidified, a yellow solid was precipitated (1.03 g.). The substance was very sparingly soluble in most organic solvents and could not be crystallised, but after being washed and dried it was almost pure; m. p. 265—267° after softening at 262° (Found: C, 70.0; H, 4.9.  $C_{23}H_{18}O_6$  requires C, 70.7; H, 4.6%.  $C_{23}H_{18}O_6 \cdot \frac{1}{2}H_2O$  requires C, 70.0; H, 4.7%). This 5 : 7-*dihydroxy-4'-benzyloxy-3'-methoxyflavone* gives a yellow-brown coloration with alcoholic ferric chloride.

5 : 7 : 4'-*Trihydroxy-3'-methoxyflavone* (II).—The benzyl derivative last described (0.8 g.) was suspended in acetic acid (45 c.c.), heated on the steam-bath, and treated gradually with concentrated hydrochloric acid (3 c.c.). After 10 minutes, a further quantity (1.5 c.c.) of concentrated hydrochloric acid was added, and the heating

continued for 30 minutes; the mixture was finally boiled. The solution was decanted from a small unattacked residue, and, on addition of water (30 c.c.), gave a flocculent yellow precipitate, which was collected and dried (0.5 g.) (Found: C, 63.9; H, 4.4; MeO, 10.3%). This product was acetylated in the usual manner and gave 0.4 g., m. p. 212°, which, crystallised from ethyl acetate, formed soft white needles, m. p. 220—221° (0.35 g.; recrystallised, 0.29 g., m. p. 220—221°) (Found: C, 61.9; H, 4.4.  $C_{22}H_{18}O_9$  requires C, 62.0; H, 4.2%).

On hydrolysis by means of alcoholic potassium hydroxide, 5:7:4'-triacetoxy-3'-methoxyflavone gave in the first place bright yellow needles of the potassium salt of the trihydroxymethoxyflavone; these were collected and dissolved in water and afforded on acidification the pure flavone, m. p. 328—330°, as a yellow precipitate (Found in material dried in a vacuum: C, 62.8; H, 4.2; MeO, 9.3.  $C_{16}H_{12}O_6 \cdot \frac{1}{2}H_2O$  requires C, 62.7; H, 4.2; 1MeO, 9.5%). This very sparingly soluble substance crystallised from nitrobenzene in yellow prismatic needles, m. p. 330—331° (Found: C, 63.9; H, 3.9; MeO, 9.8.  $C_{16}H_{12}O_6$  requires C, 64.0; H, 4.0; 1MeO, 9.7%). Like diosmetin, the flavone is a very weak mordant dye. It is much more sparingly soluble and intensely coloured than is diosmetin.

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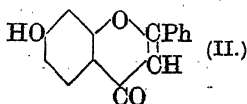
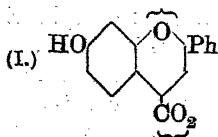
[Received, February 20th, 1930.]

### CIX.—*Anthoxanthins. Part XII. Transition from a Flavylum Salt to a Flavone, illustrated by a New Synthesis of Scutellarein Tetramethyl Ether.*

By ROBERT ROBINSON and GEROLD SCHWARZENBACH.

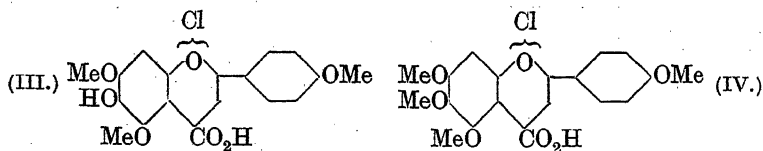
ALTHOUGH the pyrones stand in the relation to the pyrylium salts that the pyridones bear to the alkylpyridinium salts, and although the latter can be very readily changed to the pyridones by oxidation, yet there are surprisingly few recorded examples of the production of pyrones by direct or indirect processes from members of the pyrylium group.

Bülow and Wagner (*Ber.*, 1903, 36, 1941) found an isolated example in the oxidation of 7-hydroxy-4-carboxyflavylum betaine



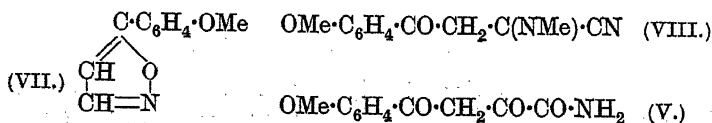
(I) (formulated previously as a pyranol) to 7-hydroxyflavone (II) by means of chromic acid in acetic acid solution. This we have confirmed, but, although the conditions have been somewhat improved, the yield of the flavone remains highly unsatisfactory.

Moreover, the reaction is not a general one, and proposed applications to the synthesis of scutellarein failed. *Anisoylpyruvic acid*,  $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , obtained by the usual method, has been condensed with 2 : 6-dimethoxyquinol and with antiarol in the presence of hydrogen chloride, furnishing the flavylum salts (III) and (IV), respectively.



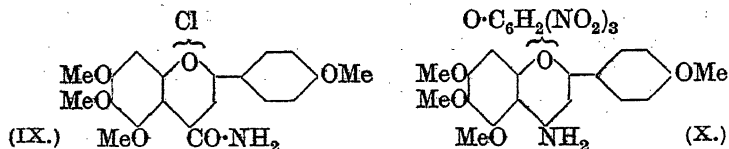
In spite of various attempts, neither these salts nor the related *betaines* could be oxidised to scutellarein derivatives. It was, however, possible to achieve our object indirectly by applying the Hofmann reaction to the amide of the acid (IV). The chief difficulty was the preparation of the required *anisoylpyruvamide* (V). If a convenient method of preparation of compounds of this type could be devised, the new flavone synthesis now to be described might acquire considerable importance, since it is applicable to certain types of structure not readily built up by hitherto known processes. Some of the more obvious routes to the *aroylpyruvamide*s have been tested without success, and we were forced back upon an interesting but indirect series of reactions due to Mumm and Münchmeyer (*Ber.*, 1910, **43**, 3335), who obtained benzoylpyruvamide. The stages in the present case were the following :

Anisoylacetaldehyde (Pratt, Robinson, and Williams, J., 1924, **125**, 202) was converted into its *oxime*,  $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NOH}$  (VI), and this was dehydrated by the action of acetyl chloride, giving 5-anisylisooxazole (VII). The *methosulphate* of this base reacted with potassium cyanide in aqueous solution with formation of  $\alpha$ -methylimino- $\beta$ -anisoylpropionitrile (VIII), which was hydrolysed to anisoylpyruvamide (V) by means of dilute hydrochloric acid.

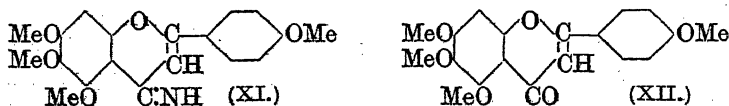


Anisoylpyruvamide and antiarol with the help of hydrogen chloride yielded a product containing 4-carbamyl-5 : 6 : 7 : 4'-tetramethoxyflavylium chloride (IX), and this, on treatment with potassium

hypochlorite and potassium hydroxide in methyl-alcoholic solution, reacting doubtless as the pseudo-base, gave another pseudo-base



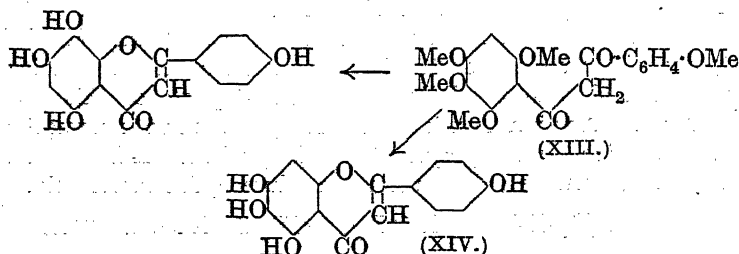
which could be transformed into 4-amino-5:6:7:4'-tetramethoxyflavylum picrate (X). The corresponding base is, doubtless, the flavone-imine (XI), and the tetramethoxyflavone (XII) resulted when the imine was treated with boiling dilute aqueous sodium hydroxide. The existence of the flavone-imine recalls that of a xanthone-imine obtained by the condensation of phloroglucinol with salicylonitrile under the conditions of the Hoesch reaction (Nishikawa and Robinson, J., 1922, 121, 839); the resistance to hydrolysis by acids and



other properties are parallel in the two series.

The substance (XII) had the melting point and other properties of scutellarein tetramethyl ether (Molisch and Goldschmiedt, *Monatsh.*, 1910, 31, 439), and we were able to establish the identity by direct comparison with a specimen prepared from scutellarein. For providing the latter, we are greatly indebted to Professor E. Späth and Dr. F. Wessely.

Scutellarein has been previously synthesised by Bargellini (*Gazzetta*, 1915, 45, 69), who submitted pentamethoxydibenzoylmethane (XIII) to the action of hydriodic acid; the reaction might have



proceeded in the two directions indicated. Actually, scutellarein (XIV) was produced and the reaction was correctly interpreted in the light of certain analogies. The present unambiguous synthesis confirms these deductions and supplies a proof of the constitution of scutellarein.

## EXPERIMENTAL.

*7-Hydroxy-4-carboxyflavylium Derivatives.*—Bülow and Wagner (*loc. cit.*) did not crystallise the chlorides obtained by the condensation of resorcinol, benzoylpyruvic acid or its ester, and hydrogen chloride, so the following data may be recorded.

7-Hydroxy-4-carboxyflavylium betaine (I) decomposes at 248°, the corresponding picrate decomposes at 226°; on solution in ethyl-alcoholic hydrogen chloride and gradual addition of ether, *7-hydroxy-4-carboxyflavylium chloride* (decomp. 250°) crystallised in orange-red leaflets (Found: Cl, 11.6.  $C_{18}H_{11}O_4Cl$  requires Cl, 11.7%).

7-Hydroxy-4-carbethoxyflavylium picrate decomposes at 225° and similarly yields *7-hydroxy-4-carbethoxyflavylium chloride*, orange leaflets decomposing at 198° (Found: Cl, 10.2.  $C_{18}H_{15}O_4Cl$  requires Cl, 10.5%).

The oxidation of the betaine to 7-hydroxyflavone does not proceed satisfactorily; a slight improvement followed on the adoption of the following conditions:

A solution of chromic anhydride (0.7 g.) in water (10 c.c.) was added to one of 7-hydroxy-4-carboxyflavylium betaine (0.7 g.) in hot 25% sulphuric acid (30 c.c.); carbon dioxide was then briskly evolved and an orange precipitate (0.45 g.) was formed. After crystallisation, 7-hydroxyflavone (0.15 g., m. p. 240°) was obtained.

Our further experience has shown that this is a special case, and the reaction is by no means a general one. It fails in the scutellarein series described below.

*Anisoylpyruvic Acid and its Ethyl Ester.*—A mixture of *p*-methoxyacetophenone (79 g.) and ethyl oxalate (77 g.) was added to a solution of sodium ethoxide (25 g. of sodium) in alcohol (400 c.c.), the whole refluxed for  $\frac{1}{2}$  hour, and the alcohol evaporated. An aqueous solution of the residue was saturated with carbon dioxide and filtered, and the crude acid (64 g.) precipitated by the addition of hydrochloric acid. This substance crystallised from alcohol in pale brown needles or irregular prisms, decomp. at 162.5° (Found: C, 54.9; H, 5.0; loss at 110° in a vacuum, 7.6.  $C_{11}H_{10}O_5 \cdot H_2O$  requires C, 55.0; H, 5.0;  $H_2O$ , 7.5%). The yield can be improved by carrying out the condensation in the cold and subsequently hydrolysing the ester, but this is hardly worth doing.

A mixture of *p*-methoxyacetophenone (13.5 g.), ethyl oxalate (13 g.), sodium ethoxide (from 2 g. of sodium) and alcohol (35 c.c.) was kept for 12 hours at 0° and then added to ether. The cake of sodium derivative was collected and decomposed at 0° in aqueous solution with carbon dioxide (yield, 16 g.).

*Ethyl anisoylpyruvate* crystallised from alcohol in colourless

prisms, m. p.  $54^{\circ}$  (Found : C, 62.3; H, 5.7.  $C_{13}H_{14}O_5$  requires C, 62.3; H, 5.6%).

6-*Hydroxy-5:7:4'-trimethoxy-4-carboxyflavylum Derivatives* (Chloride, III).—A solution of 2:6-dimethoxyquinol (4.25 g.) and anisoylpyruvic acid (5.6 g.) in acetic acid (50 c.c.) was saturated with hydrogen chloride at  $90-100^{\circ}$  for 1 hour, then cooled to  $0^{\circ}$ , and ether (150 c.c.) added without interrupting the passage of hydrogen chloride. The dark red solid was collected (5.8 g.), and a portion converted into the *picrate* in hot alcoholic solution by the addition of picric acid; the derivative crystallised immediately in dark red leaflets which decomposed at  $224^{\circ}$  (Found : C, 49.6; H, 3.8; N, 7.2.  $C_{25}H_{19}O_{14}N_3 \cdot H_2O$  requires C, 49.7; H, 3.5; N, 6.9%). This *picrate* was suspended in pure methyl alcohol and hydrogen chloride introduced until it dissolved; on the addition of ether, the chloride crystallised in dark red needles, decomposing at  $170-180^{\circ}$  and readily soluble in water and alcohol.

Another portion of the crude chloride was dissolved in hot aqueous sodium acetate, and the filtered solution acidified with acetic acid. The *betaine* separated in red needles, and the substance could be recrystallised from alcohol, forming very small, green prisms, decomp.  $182^{\circ}$  (Found : C, 59.6; H, 5.0.  $C_{19}H_{16}O_7 \cdot 1\frac{1}{2}H_2O$  requires C, 59.6; H, 5.0%), sparingly soluble in water and giving a bright orange solution in sulphuric acid.

5:6:7:4'-*Tetramethoxy-4-carboxyflavylum Derivatives* (Chloride, IV).—A solution of antiarol (9.2 g.) and anisoylpyruvic acid (11.6 g.) in acetic acid (60 c.c.) was saturated with hydrogen chloride at  $100^{\circ}$  for 3 hours, cooled, and dry ether (200 c.c.) added, hydrogen chloride being passed meanwhile. After being kept at  $0^{\circ}$  for 12 hours, the solid was collected (21 g., air-dried) and this chloride was converted into the *betaine* by solution in aqueous sodium acetate and acidification with acetic acid. The orange needles obtained were readily soluble in water and could be recrystallised from alcohol in a similar form, m. p.  $127-130^{\circ}$  (Found : C, 59.8; H, 5.6. Found in material dried at  $100^{\circ}$  in a vacuum: C, 65.1; H, 5.2.  $C_{26}H_{18}O_7 \cdot 1\frac{1}{2}H_2O$  requires C, 60.4; H, 5.3%.  $C_{20}H_{18}O_7$  requires C, 64.9; H, 4.9%).

The related *picrate* crystallised from alcohol in deep orange needles, decomp.  $204-205^{\circ}$  (Found : C, 50.4; H, 4.1; N, 7.1.  $C_{26}H_{21}O_{14}N_3 \cdot H_2O$  requires C, 50.6; H, 3.7; N, 6.8%).

The oxidising agents tested with the object of preparing *O*-tetramethylscutellarein were chromic acid in acetic acid and dilute sulphuric acid solutions, persulphate in dilute sulphuric acid, lead peroxide and acetic acid, manganese dioxide and dilute sulphuric acid and hydrogen peroxide in acetic acid, and finally potassium



ferricyanide in neutral and in alkaline solution; in all cases, the results were negative.

The action of phosphorus pentachloride on the betaine appeared to proceed normally, giving the acid chloride flavylum chloride, but the action of ammonia or hydrazine on this derivative did not give the anticipated results.

*Anisoylacetaldoxime* (VI).—The sodium salt of  $\omega$ -hydroxy-methylene-*p*-methoxyacetophenone (45 g.) (Pratt, Robinson, and Williams, *loc. cit.*) was dissolved in ice-water (600 c.c.), and hydroxylamine hydrochloride (25 g.) in water (50 c.c.) added; separation of the *oxime* began immediately. The substance (yield, 25 g.) crystallised from benzene in colourless microscopic needles, m. p. 120° (Found: C, 62.4; H, 5.7; N, 7.4.  $C_{10}H_{11}O_3N$  requires C, 62.3; H, 5.7; N, 7.3%). It retained benzene tenaciously, and the determination of nitrogen was carried out with a specimen giving C, 63.3; H, 5.6%, and probably containing a trace of the solvent.

*5-Anisylisooxazole* (VII).—Claisen (*Ber.*, 1891, 24, 132) has shown that the dehydration of the *oxime* of benzoylacetaldehyde with acetyl chloride yields phenylisooxazole, whereas the use of acetic anhydride leads to the formation of  $\omega$ -cyanoacetophenone, which is also obtained by the action of alkalis on phenylisooxazole.

Finely powdered anisoylacetaldoxime (10 g.) was added to acetyl chloride (10 g.) with cooling; a vigorous reaction and brisk evolution of hydrogen chloride ensued. The excess of the reagent was removed by evaporation and the oily residue was mixed with 3% sodium hydroxide solution (150 c.c.); the oil then quickly solidified. The product crystallised from 80% alcohol (100 c.c.) in almost colourless, flat prisms, m. p. 63° (yield, 7.5 g.) (Found: C, 68.7; H, 5.1; N, 8.0.  $C_{10}H_9O_2N$  requires C, 68.7; H, 5.1; N, 8.0%). On boiling for 5 minutes with alcoholic sodium hydroxide, *5-anisylisooxazole* was transformed into the isomeric  $\omega$ -cyano-*p*-methoxyacetophenone, which crystallised from alcohol in colourless needles, m. p. 131° (Found: C, 68.9; H, 5.2; N, 8.1%) in good agreement with the statement of Bargellini (*Gazzetta*, 1911, 41, 748), who prepared the compound in another way.

The *methosulphate* was obtained by heating a mixture of anisylisooxazole (8.9 g.) and pure methyl sulphate (5.3 g.) on the steam-bath. Reaction occurred at about 90° and soon afterwards the whole crystallised with evolution of heat. The salt was washed with acetone and separated on the addition of ether to its alcoholic solution in bright yellow crystals, m. p. 142.5° (Found: N, 4.5; S, 10.4.  $C_{12}H_{15}O_6NS$  requires N, 4.7; S, 10.6%). The golden-yellow picrate has m. p. 147.5°.

$\alpha$ -Methylimino- $\beta$ -anisoylpropionitrile (VIII).—Potassium cyanide

(5 g.) in water (50 c.c.) was very gradually added to a solution of anisylisooxazole methosulphate (6.5 g.) in ice-cold water (50 c.c.). The precipitate obtained (4.5 g.) consisted of the pure *nitrile*, m. p.  $109^{\circ}$  (not raised by crystallisation); it separated from alcohol in pale yellow needles or well-shaped prisms (Found: C, 66.6; H, 5.6; N, 13.0.  $C_{12}H_{12}O_2N_2$  requires C, 66.8; H, 5.6; N, 13.0%). The solution in sulphuric acid had a dark purple colour. Experiments on the condensation of this substance with antiarol had no definite outcome.

*Anisoylpyruvamide* (V).—Anisoylpyruvic acid could not be directly converted into its amide either by way of the chloride or through the ester by means of ammonia. Nor could the amide be obtained by the condensation of ethyl oxamate and *p*-methoxyacetophenone.

Methyliminoanisoylpropionitrile (23 g.) was powdered and agitated with *N*-hydrochloric acid (500 c.c.) for 36 hours, and the product isolated (19 g.). The *amide* was sparingly soluble in hot ethyl alcohol and crystallised from *isoamyl* alcohol in colourless microscopic needles, decomp.  $192^{\circ}$  (Found: C, 59.8; H, 5.2; N, 6.0.  $C_{11}H_{11}O_4N$  requires C, 59.7; H, 5.0; N, 6.3%). The solution in sulphuric acid was reddish-brown. The substance, when boiled with concentrated hydrochloric acid, was hydrolysed to anisoylpyruvic acid.

The acid mother-liquor from the preparation described above contained 10% more than the theoretical amount of volatile bases, so it might be advantageous to interrupt the process at an earlier stage. There was also a considerable loss on crystallisation of the crude product.

*4-Carbamyl-5:6:7:4'-tetramethoxyflavylium Chloride* (IX).—Owing to the very great ease with which the amide group in this salt is hydrolysed, we have not obtained a pure specimen of the substance, but a product which must consist of it to a large extent was prepared in the following manner.

Hydrogen chloride was led into a solution of antiarol (7.0 g.) and anisoylpyruvamide (8.0 g.) in purified acetic acid at  $70^{\circ}$  for  $1\frac{1}{2}$  hours; ammonium chloride separated. The mixture was cooled and kept saturated with hydrogen chloride for 24 hours, then diluted with ether and kept in the ice-chest for 4 hours. The product was washed with ether and dried at  $100^{\circ}$  in a vacuum, giving a dark brownish-red mass with a green reflex (9.5 g.). Attempts to isolate the picrate of the amide gave only the already described tetramethoxycarboxyflavylium picrate, which crystallised from acetic acid in an anhydrous condition (Found: C, 52.1; H, 3.9; N, 7.1.  $C_{26}H_{21}O_{14}N_3$  requires C, 52.1; H, 3.5; N, 7.0%). The identity of this picrate with the substance previously obtained was proved by a comparison

of colour reactions and decomposition points, and the related chloride was prepared and found to be free from nitrogen.

*4-Amino-5:6:7:4'-tetramethoxyflavylium Picrate* (X).—The crude chloride (9.5 g.) obtained as described in the last section was dissolved in methyl alcohol (75 g.) and cooled to 0°, a cooled solution of potassium hypochlorite (33 c.c. from 1.77 g. of chlorine, 4.82 g. of potassium hydroxide, and water) added, and the mixture heated on the steam-bath for  $\frac{1}{2}$  hour. Acetic acid (50 c.c.) and a solution of picric acid (12 g.) in acetic acid (100 c.c.) were successively introduced; a yellow *picrate* crystallised on cooling, and this was collected and washed with acetic acid and ether (yield, 4.8 g. in this experiment, but much less when more alkali was employed). The salt crystallised from acetic acid in flat golden-yellow prisms (3.0 g.), very sparingly soluble in all solvents and decomposing at 281° (Found: C, 52.6; H, 4.0; N, 9.7.  $C_{25}H_{22}O_{12}N_4$  requires C, 52.6; H, 4.1; N, 9.8%). The corresponding chloride was obtained in pale pink needles by passing hydrogen chloride into a suspension of the *picrate* in acetic acid and adding ether. The base obtained on treatment with aqueous sodium hydroxide was a sticky, very pale yellow precipitate.

*5:6:7:4'-Tetramethoxyflavone (Scutellarein Tetramethyl Ether)* (XII).—*4-Amino-5:6:7:4'-tetramethoxyflavylium chloride* (0.7 g.) was refluxed with 10% sodium hydroxide solution (7 c.c.) for 45 minutes, ammonia being evolved and the substance becoming a dark brown oil. When this was washed with very dilute hydrochloric acid, it became solid and bright yellow; the substance crystallised from alcohol (charcoal) in thick colourless prisms (S), m. p. 161° (Found: C, 66.9; H, 5.6. Calc. for  $C_{19}H_{18}O_6$ : C, 66.6; H, 5.3%).

The crude *scutellarein* kindly supplied by Professor Späth was methylated by means of an excess of methyl sulphate and 15% sodium hydroxide solution in presence of acetone; the impurities formed as a result of oxidation were insoluble in ether, and, when the washed and dried extract was concentrated to a small bulk, *scutellarein tetramethyl ether* crystallised in colourless prisms. After one crystallisation from alcohol, the specimen (N) had m. p. 161°, undepressed by admixture with an equal amount of (S).

The two specimens had identical properties and gave indistinguishable yellow to orange solutions in mineral acids of various concentrations. Very characteristic is the fact that the ether is partly extracted from ethereal solution even by 2% hydrochloric acid, and that it dissolves in hot 10% hydrochloric acid to a yellow solution, from which the hydrochloride separates as a mass of woolly yellow needles on cooling. On addition of mercuric chloride to the hot solution of the hydrochloride, there is an immediate pre-

cipitation of the very sparingly soluble, pale yellow mercurichloride. The microscopic appearance of the crystals of (S) and (N) and of their hydrochlorides was the same, and the solubility properties also were compared.

The methoxyl content of *O*-tetramethylscutellarein should be 36.25%, but a Zeisel-Pregl estimation gave MeO, 34.22%, and even a Herzig-Meyer-Pregl estimation gave only MeO, 34.7%. Apparently, a fraction of the methyl attached to oxygen is transferred to carbon in the course of the demethylation process.

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CX.—*Strychnine and Brucine. Part X. The Degradation of Dinitrostrycholcarboxylic Acid: its Recognition as a Derivative of Quinoline and the Consequent Modifications of the Constitutional Formulae for the Strychnos Bases proposed in Part VII.*

By KOTTIAZATH NARAYANA MENON, (the late) WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

UNEXPECTEDLY, the esterification of dinitrostrycholcarboxylic acid (Tafel, *Annalen*, 1898, **301**, 336; compare Part IX, this vol., p. 382) with ethyl alcohol and a mineral acid catalyst affected two hydroxyl groups and afforded *ethyl dinitro-O-ethylstrycholcarboxylate*,  $C_9NH_2(NO_2)_2(OH)(OEt) \cdot CO_2Et$  (I). This ester reacted with hydrazine in the normal manner, yielding the *hydrazide*,  $C_9NH_2(NO_2)_2(OH)(OEt) \cdot CO \cdot NH \cdot NH_2$  (II), and the further stages of the Curtius reactions also gave good results, the *urethane*,  $C_9NH_2(NO_2)_2(OH)(OEt) \cdot NH \cdot CO_2Et$  (III), being the final product.

It will be recalled that dinitrostrycholcarboxylic acid cannot be degraded by boiling with nitric acid; this urethane, however, in which  $\cdot NH \cdot CO_2Et$  replaces  $\cdot CO_2H$ , is readily attacked by the reagent and yields picric acid.

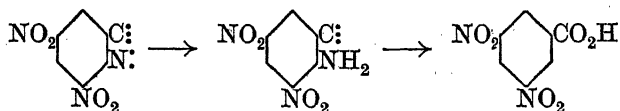
This result is inconsistent with the suggestion that strychol is a dihydroxyisoquinoline, because derivatives of this series would undoubtedly yield trinitro-*m*-hydroxybenzoic acid and not picric acid.

We have examined the behaviour of *m*-hydroxybenzaldehyde

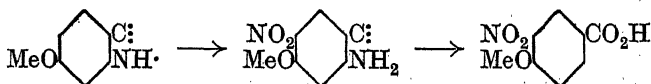
and *m*-hydroxybenzoic acid with boiling nitric acid, and no trace of picric acid could be detected by the sensitive potassium salt method of isolation.

Further, if strychol is thus to be recognised as a dihydroxyquinoline, the formation of picric acid proves that both hydroxyl groups are in the pyridine nucleus, in view of the fact established in Part IX (*loc. cit.*) that the quinoline nitrogen always furnishes a hydroxyl group in the oxidation-nitration process.

Furthermore, Mr. J. Resuggan, to whom we are greatly indebted for undertaking the preparation of large quantities of dinitrostrycholcarboxylic acid, has isolated a by-product of the oxidation of strychnine with nitric acid. This we have identified as 3:5-dinitrobenzoic acid, and its formation is evidently due to elimination of an amino-group in accordance with the scheme :

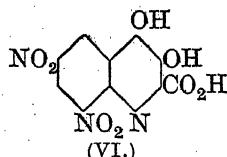
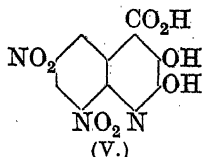
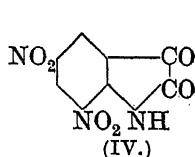


An analogous reaction is that involved in the production of nitroanisic acid from harmaline by oxidation with nitric acid (O. Fischer and Boesler, *Ber.*, 1912, 45, 1934) :



Confirmation was obtained in the transformation of the urethane (III) into 5:7-dinitroisatin (IV), which was accomplished by hydrolysis with sulphuric acid and subsequent oxidation by permanganate in acid solution. This dinitroisatin does not appear to have been previously prepared and has been obtained in good yield by the nitration of isatin in sulphuric acid solution.

In Part IX, it was clearly proved that strychol is not 2:4-dihydroxyquinoline, and therefore dinitrostrycholcarboxylic acid must be represented by one of the formulæ V and VI (or a pyridone tautomeride). Either of these structures serves to accommodate



the fact established by Tafel that dinitrostrychol behaves as a monobasic acid towards potash but as a dibasic acid towards baryta.

Having found that dinitrostrycholcarboxylic acid yielded a diethyl

ester, we were led to attempt the direct esterification of dinitrostrychol, and, using methyl alcohol, we obtained with greater ease than formerly the known dinitrostrychol monomethyl ether,  $C_9NH_3(NO_2)_2(OH) \cdot OMe$ . This substance reacts with hydrazine in boiling methyl-alcoholic solution with formation of *dinitrohydrazinodeoxystrychol*,  $C_9NH_3(NO_2)_2(OH) \cdot NH \cdot NH_2$  (VII), a base which forms very sparingly soluble salts and a sparingly soluble, pale yellow *isopropylidene* derivative,  $C_9NH_3(NO_2)_2(OH) \cdot N_2H \cdot CMe_2$ . Unfortunately, the oxidation of this hydrazine with ferric chloride regenerates dinitrostrychol: other conditions, however, are in course of investigation. We are of the opinion that the acidic hydroxyl of dinitrostrychol is that in position 3, but we have not yet been able to get decisive experimental evidence on the point. Synthetical work in the 2 : 3- and 3 : 4-dihydroxyquinoline groups is in progress.

Irrespective of the outcome of these further researches, certain conclusions in regard to the constitutions of strychnine and brucine now appear to be fully justified.

The *isoquinoline* structure (Fawcett, Perkin, and Robinson, Part VII, J., 1928, 3082) was advanced mainly in order to illustrate a mode of symbolisation of the reactions of strychnine which had been developed since 1912; especially, it was desired to emphasise the ether nature of the bases, the possession of one ethylenic double bond, and a theory (*loc. cit.*, p. 3086) of the course of the degradations to strychninolone and curbine brought to light by Leuchs and his collaborators (for references, see Part VII, *loc. cit.*, p. 3085). It is unfortunate that these ideas, which we consider to be fundamentally sound, were linked with a view of the nature of dinitrostrychol-carboxylic acid, the inherent improbability of which was almost immediately disclosed by the investigations of Leuchs and of Wieland on the products obtained by breaking down the aromatic nucleus of the alkaloids.

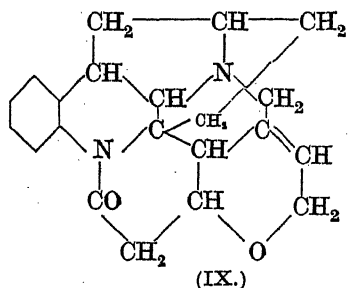
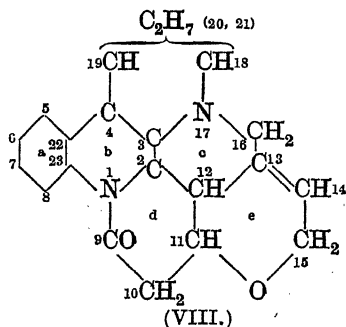
The new conception which we now bring into the discussion is that the hydroxyl in position 3 in the quinoline ring of dinitrostrycholcarboxylic acid marks the position of the b-N of strychnine; it appears to us that this hypothesis is the only one that can explain the appearance of the hydroxyl in this position.

In this connexion, we have prepared 6 : 8-dinitrohydrocarbostyryl, and have not yet succeeded in attempts to oxidise this substance in position 3 either by means of nitric acid or in other ways.

Embodying, now, the views advanced in Part VII, apart from those connected with dinitrostrycholcarboxylic acid, we find that strychnine must be represented by the expression (VIII).

All the many possibilities based on (VIII) must have a bridged

ring, shown in one plausible example (IX); the conceivable variations are obvious.



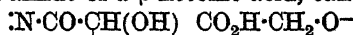
The new structure (VIII) has many advantages over earlier suggestions, and can be justified experimentally in every detail; the main points are the following:—

(1) The quinoline skeleton with b-N at 17, as already explained, gives naturally dinitrostrycholcarboxylic acid (V or VI).

(2) The N-CO group cannot be at 1, 2, because it must be expanded to  $\text{-N}\cdot\text{CO}\cdot\text{CH}_2\text{-}$  in view of the formation of benzylidene-strychnine (Part VIII, J., 1929, 967).

(3) The properties of strychnidine and most clearly of the dihydro-strychnidines (A) and (B) prove that the second oxygen atom of the bases has ether function. The attachment of the ether oxygen atom at 11 has already been discussed (Part VIII, *loc. cit.*).

(4) The new formula allows the permanganate oxidation of strychnine (Leuchs) to proceed entirely in one section of the molecule: the  $\text{N}\cdot\text{CH}_2\text{-}\overset{\cdot}{\text{C}}\text{:CH}\cdot\text{CH}_2\text{-O-}$  becomes  $\text{N}\cdot\text{CO}\cdot\overset{\cdot}{\text{C}}(\text{OH})\cdot\text{CO}\cdot\text{CH}_2\text{-O-}$ , and this, being an amide of a  $\beta$ -ketonic acid, can yield



by hydrolysis. The position chosen for b-N thus gives an excellent explanation of the formation of dihydrostrychninonic acid (and of dihydrobrucinonic acid), which is a difficulty for other formulations. Further oxidation gives strychninonic acid,  $\text{N}\cdot\text{CO}\cdot\overset{\cdot}{\text{C}}\text{O}\cdot\text{CO}_2\text{H}\cdot\text{CH}_2\text{-O-}$ .

(5) Leuchs has recently examined many strychnine (brucine) derivatives in which nucleus (a) has been broken down; almost all of these substances absorb two oxygen atoms on oxidation with bromine and water, a third oxygen atom being taken up on treatment of the product with mercuric oxide. These changes are clearly represented by the scheme:



The double bond at 13, 14 is affected in every case. This gives

important support to the view that strychnine contains the group figured at 13, 14 and, indirectly, to our theory of the course of the permanganate oxidation.

(6) The hydrogen atom at  $C_{12}$  is requisite for the transference of the double bond in the strychninolone series from 11—10 to 11—12.

(7) Some considerations respecting the reduced strychnine derivatives will be discussed in a later communication.

For the above and other reasons, we consider that the structure (VIII) is almost certainly correct; it can with some show of probability be concluded that  $C_4$  bears a hydrogen atom and that  $C_{20}$  is attached to  $C_2$ ; analogy with quinine then allows us provisionally to adopt (IX) as a working hypothesis.

The attachment of a hydrogen atom to  $C_4$  seems to be required in order to explain the nature and formation of a base  $C_{17}H_{20}O_3N_2Br_2$  which H. Leuchs, Mildbrand, and R. Leuchs (*Ber.*, 1922, 55, 2703) obtained along with Hanssen's acid,  $C_{19}H_{22}O_6N_2$ , by treating cacotheline (nitrate of nitrobruciquinone hydrate) with bromine (Hanssen, *Ber.*, 1887, 20, 452; Ciusa and Scagliarini, *Roy. Accad. Lincei*, 1910, 19, 504). On treatment with baryta, the bromo-compound yields a base,  $C_{17}H_{22}O_5N_2$  (Leuchs, *Ber.*, 1929, 62, 1929), which can be oxidised by means of chromic acid, yielding Wieland's acid,  $C_{17}H_{22}O_6N_2$ , also obtainable by the direct oxidation of brucine (Wieland and Münster, *Annalen*, 1929, 469, 216) or mono-amino- or diamino-strychnine (Leuchs and Kröhnke, *Ber.*, 1929, 62, 2176) or strychnine (Cortese, *Annalen*, 1929, 476, 280) by means of chromic acid.

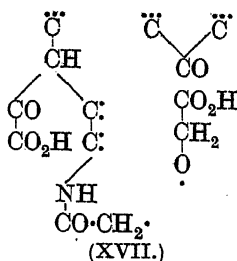
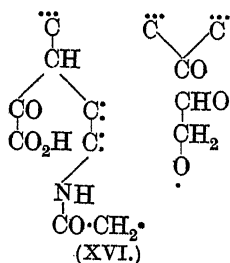
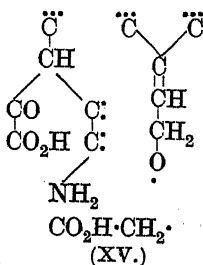
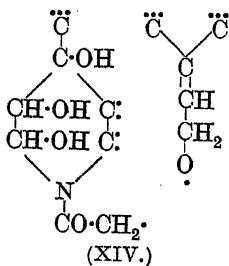
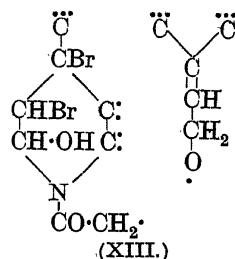
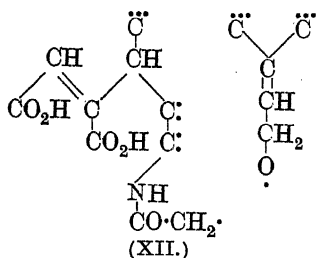
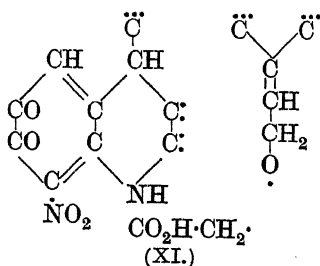
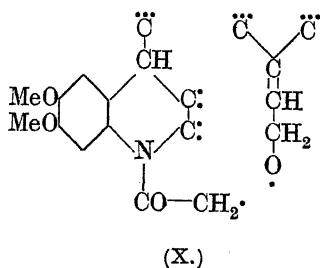
Wieland's acid appears to be a dibasic keto-acid in which the amide group is hydrolysed, and the following partial formulæ will serve best to illustrate the manner in which we envisage these complex relationships: Brucine (X) (compare Part III, J., 1925, 127, 1158), cacotheline (XI), Hanssen's acid (XII),  $C_{17}H_{20}O_3N_2Br_2$  (XIII),  $C_{17}H_{22}O_5N_2$  (XIV), Wieland's acid,  $C_{17}H_{22}O_6N_2$  (XV),  $C_{17}H_{20}O_7N_2$  by the action of bromine on XV (XVI) (Leuchs and Hoffmann, *Ber.*, 1929, 62, 2307),  $C_{17}H_{20}O_8N_2$  by the action of mercuric oxide on XVI (XVII) (Leuchs and Hoffmann, *Ber.*, 1930, 63, 440).

Even the substance (XIV), which is considered to contain an aldehyde group immobilised by internal condensation with an  $-NH\cdot CO-$  group, can be oxidised at the double bond in the usual way, yielding successively  $C_{17}H_{22}O_7N_2$  and  $C_{17}H_{22}O_8N_2$  (Leuchs, *Ber.*, 1929, 62, 1935).

The compound  $C_{17}H_{20}O_8N_2$  (XVII) can also be obtained from Hanssen's acid (XII), for example, by conversion by means of bromine into  $C_{19}H_{22}O_8N_2$ , then by mercuric oxide into  $C_{19}H_{22}O_9N_2$ .

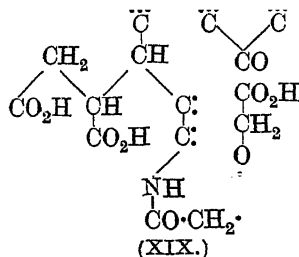
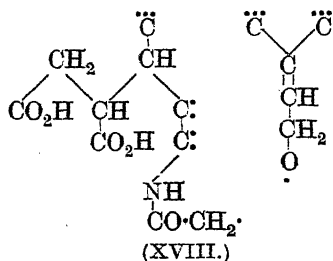


and finally by permanganate into  $C_{17}H_{20}O_8N_2$  and oxalic acid; or  $C_{19}H_{22}O_8N_2$  can be directly oxidised by permanganate (Leuchs, *Ber.*, 1925, 58, 1730; Leuchs, Bender, and Wegener, *Ber.*, 1928, 61,

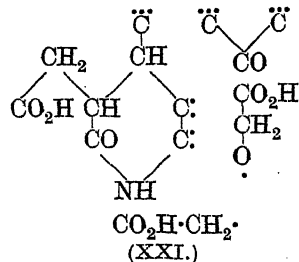
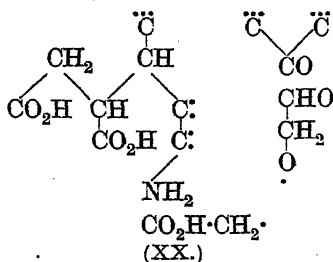


2353; Leuchs and Hoffmann, *Ber.*, 1929, 62, 1253; 1930, 63, 440). The interpretation of these changes along the lines already laid down offers no difficulties. Another important series of substances is

obtained by reducing Hanssen's acid (XII) to  $C_{19}H_{24}O_6N_2$  (XVIII) by means of sodium amalgam (Leuchs, *Ber.*, 1929, 62, 1929).



Permanganate changes the reduced Hanssen's acid to  $C_{19}H_{24}O_9N_2$  (XIX) (Leuchs and Kröhnke, *Ber.*, 1929, 62, 2599), and it is very interesting that an isomeride has been obtained from (XVIII) by using bromine and then either mercuric oxide or permanganate. The explanation seems to be that the amide ring opens and closes again in a new position; the intermediate is then  $C_{19}H_{26}O_9N_2$  (XX) and the isomeric  $C_{19}H_{24}O_9N_2$  would be (XXI) (Leuchs, Mildbrand, and Leuchs, *Ber.*, 1922, 55, 2412; Leuchs and Kröhnke, *Ber.*, 1929, 62, 2599).



Again, the Hanssen  $C_{16}$ -acid,  $C_{16}H_{20}O_4N_2$ , which Wieland and Münster (*loc. cit.*) obtained along with the Wieland acid by the oxidation of brucine with chromic acid also takes up two oxygen atoms on oxidation with bromine and a third on subsequent treatment with mercuric oxide (Leuchs and Hoffmann, *Ber.*, 1930, 63, 446).

On the basis of these formulæ, we are able to predict that the substances (XVII), (XIX), (XXI) and the acid  $C_{16}H_{20}O_7N_2$  from the Hanssen  $C_{16}$ -acid should contain a  $-CH_2 \cdot CO_2H$  fragment detachable in the form of glycollic acid or a derivative under the appropriate conditions.

The above formulæ require in some cases that the molecule should contain more carbonyl groups than have been experimentally recognised, but this is not unusual and in our experience strychnidone

(Clemons, Perkin, and Robinson, J., 1927, 1589) gave a disemicarbazone, but the analogous brucidone (Gulland, Perkin, and Robinson, *ibid.*, p. 1627) gave only a monosemicarbazone. Similar remarks apply to the number of carboxyl groups, but, broadly, the agreement between theory and experiment is remarkable.

Returning to a consideration of (VIII), the attachment of one of the carbons of the bridge ring to carbon at position 2 seems reasonable in view of the stability of Wieland's acid (XV) to chromic acid, and because there are reasons for attributing blocked hydroaromatic character to both ring B and ring D and (2) is the common position.

It is hoped that experimental evidence bearing on this aspect of the problem will shortly be submitted to the Society.

The provisional formula (IX) contains the whole of the cinchonine skeleton of carbon and nitrogen atoms and, of course, two carbon atoms more. This is probably going too far in the search for analogies, but there is evidently some underlying relation between the two alkaloids.

It must be clearly stated that the formulæ (XI—XXI) given above are based on relations established by Leuchs in a series of brilliant investigations. For example, he has described in words the precise connexion between Hanssen's acid and Wieland's acid which is illustrated in our formulæ. It has, however, never been previously suggested that the whole series can be correlated by means of definite constitutional formulæ, and, having developed expressions for the alkaloids, it was necessary for us to show that such correlation is feasible.

#### EXPERIMENTAL.

*Ethyl Dinitro-O-ethylstrycholcarboxylate* (I).—Dinitrostrycholcarboxylic acid was refluxed for 7 hours with a large excess of 5% alcoholic sulphuric acid, and the product collected after the addition of water. It was washed with aqueous sodium carbonate and then with water, and crystallised from alcohol in almost colourless, soft needles, m. p. 111—112° (Found: C, 48.0; H, 3.9; EtO, 25.5.  $C_{14}H_{13}O_8N_2$  requires C, 47.9; H, 3.7; 2EtO, 25.6%). The ester is insoluble in aqueous sodium carbonate; on heating with aqueous sodium sulphite, yellow, orange and blood-red solutions are successively obtained.

*O-Ethyl dinitrostrycholcarbohydrazide* (II).—Ethyl O-ethyl dinitrostrycholcarboxylate (1 g.) was dissolved in the minimum quantity of boiling alcohol, and 95% hydrazine hydrate (1.6 g.) added; a yellow solid separated within a few minutes from the deep red solution and, after heating on the steam-bath for 15 minutes, the product was collected and thoroughly washed with alcohol (yield,

1.0 g.). The *hydrazide* crystallised from alcohol in pale yellow, woolly needles, m. p. 218—219° (decomp.) (Found: C, 43.1; H, 3.4; N, 20.5.  $C_{12}H_{11}O_7N_5$  requires C, 42.7; H, 3.3; N, 20.8%).

This derivative is moderately readily soluble in alcohol; addition of water to its solution in acetic acid gives a precipitate of the free base. The hydrochloride is sparingly soluble in dilute hydrochloric acid, but dissolves on heating, and addition of acetone causes a rapid separation of the *isopropylidene* derivative in colourless needles. The hydrazide is insoluble in aqueous sodium carbonate.

*Dinitrostrychylurethane* (III).—*O*-Ethyldinitrostrycholcarbohydrazide (0.5 g.) was dissolved in acetic acid (60 c.c.), and powdered sodium nitrite (0.5 g.) added to the cooled solution; shortly afterwards, the whole was poured into water (250 c.c.) and the precipitated azide was collected and dried in a vacuum. This substance melted with decomposition at 110° and dissolved slowly in aqueous sodium carbonate, doubtless as the result of hydrolysis.

The azide was added to excess of alcohol, and the mixture boiled until evolution of nitrogen ceased. The product crystallised from acetic acid in clusters of yellow needles, m. p. 199—200° (yield, 2.1 g. of the pure substance from 4 g. of the hydrazide) (Found: C, 45.9; H, 3.9; N, 15.7.  $C_{14}H_{14}O_8N_4$  requires C, 45.8; H, 3.8; N, 15.3%). This *urethane* is sparingly soluble in most organic solvents and is insoluble in aqueous sodium carbonate. It is unaffected by bromine in boiling acetic acid solution. Dilute aqueous sodium hydroxide causes the crystals to become orange and, on heating, an orange solution is obtained from which hydrochloric acid precipitates an orange-brown substance.

*Degradation of dinitrostrychylurethane.* (A) Nitric acid (40 c.c., *d* 1.42) was heated to about 60° and the urethane (1 g.) added; the mixture was then gently heated until a vigorous reaction set in, accompanied by evolution of nitrous fumes. When this ceased, the solution was boiled and concentrated to a small bulk. The picric acid formed was isolated as its sodium salt, regenerated, and identified after crystallisation by its properties and by its m. p. and mixed m. p. 122°.

(B) The urethane (1 g.) was dissolved in concentrated sulphuric acid (25 c.c.), and the yellow solution heated over a free flame until a rapid evolution of gas occurred and slackened. The yellow colour disappeared simultaneously and a dull purplish-brown colour replaced it. Water was then added drop by drop to the hot solution until the liquid was diluted to 200 c.c. *N*/10-Potassium permanganate was rapidly added to the hot solution until an excess appeared, and then a further volume (100 c.c.) was added and the mixture heated until the oxidising agent was reduced. The solution

was filtered from an insoluble orange-brown substance, cooled, and thoroughly extracted with ether.

The extract was dried with sodium sulphate and the solvent removed, leaving a yellow residue which crystallised from pure benzene and then from acetic acid in bright yellow plates, m. p. 209—210°, and at the same temperature when mixed with 5:7-dinitroisatin prepared by the method described below. The characteristic properties of the dinitroisatin were all exhibited by this specimen.

By means of the sodium sulphite and indophenine colour reactions, the formation of dinitroisatin from dinitrostrychol derivatives by many different methods was indicated. For example, it is produced by the direct oxidation of dinitrostrychol, but the yield in this case is very unsatisfactory.

If the dilute sulphuric acid solution obtained by the hydrolysis of the urethane is neutralised with ammonia, an orange base is precipitated, and this can be redissolved in dilute hydrochloric acid to a yellow solution. Addition of nitrite slightly intensifies the colour, and the diazonium salt produced couples with  $\beta$ -naphthol to give a crimson azo-compound. It is very remarkable that this base can itself be coupled with diazo-salts to give quite intensely coloured substances, the nature of which is obscure. For example, *p*-nitrobenzenediazonium acetate yields a brick-red substance which behaves like an azo-compound. The anomaly arises from the circumstance that, according to our views, there is no free position in the nucleus containing the amino-group. Addition of a little nitrite to a weakly acid solution of the amine produces a violet precipitate which is due to the diazotisation of a part of the base and coupling with the remainder; this can be proved by separating the reactions. Oxidation of acid solutions of the amine from the urethane by ferric chloride and other mild reagents gives quantitatively a reddish-brown, sparingly soluble substance, apparently of indigoid or indirubinoid nature.

*5:7-Dinitroisatin* (IV).—A solution of isatin (5 g.) in sulphuric acid (50 c.c.) was cooled to 0°, and potassium nitrate (10 g., yield poor; 25 g., yield 56%; 50 g., yield almost quantitative) added in small portions so that the temperature did not rise above 15°. The mixture was then heated at 50—55°, until a sample diluted with water gave no precipitate (about 3 hours), cooled, and poured on ice. The solution was extracted five times with ether (200 c.c. on each occasion), the combined extracts were washed free of mineral acid by means of aqueous sodium bicarbonate and dried by means of magnesium sulphate, and the ether was distilled, leaving a yellow solid residue. This substance is sparingly soluble in benzene and

crystallises therefrom in yellow prisms, or from acetic acid in bright canary-yellow, microscopic plates, m. p. 209—210° (Found : C, 40.7; H, 1.4; N, 17.7.  $C_8H_3O_6N_3$  requires C, 40.5; H, 1.3; N, 17.7%). This isatin derivative exhibits a very strong indophenine reaction and, when treated with aqueous sodium sulphite, it develops a characteristic, stable, bluish-red coloration.

It dissolved in aqueous sodium carbonate to an orange solution, the colour of which quickly faded and a colourless crystalline sodium salt separated. On boiling with aqueous sodium hydroxide, ammonia was evolved and the solution doubtless then contained a dinitrohydroxyphenylglyoxylate. Dinitroisatin (0.5 g.) was boiled with nitric acid (25 c.c., *d* 1.42), and the liquid concentrated to a small bulk : picric acid, m. p. 122°, undepressed by admixture with an authentic specimen, was isolated from the product.

6 : 8-Dinitrohydrocarbostyryl,  $(NO_2)_2C_6H_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{NH} - \text{CO} \end{smallmatrix}$ —A mixture of *o*-nitrobenzaldehyde (10 g.), malonic acid (15 g.), pyridine (100 c.c.), and piperidine (2 c.c.) was heated on the steam-bath for 30 minutes and then boiled for 30 minutes. On the addition of water and hydrochloric acid, pure *o*-nitrocinnamic acid was precipitated in almost theoretical yield.

The process of Friedländer and Weinberg (*Ber.*, 1882, 15, 1423) for the preparation of hydrocarbostyryl from ethyl *o*-nitrocinnamate works equally well with the acid, and hydrocarbostyryl is readily accessible in this way.

The nitration (of 1 mol.) was accomplished by adding sodium nitrate (5 mols.) to a solution in sulphuric acid, and completing the reaction by heating on the steam-bath. The substance crystallised from acetic acid in stout colourless needles, m. p. 175° (Found : C, 45.7; H, 3.1; N, 17.6. Calc. for  $C_9H_7O_5N_2$  : C, 45.6; H, 2.9; N, 17.7%).

The dinitrohydrocarbostyryl, m. p. 177°, obtained by van Dorp (*Rec. trav. chim.*, 1904, 23, 304) by the action of boiling dilute hydrochloric acid on a  $\beta$ -(dinitroaminophenyl)propionic acid is doubtless identical with our compound; van Dorp records that the m. p. was about 165°, raised to 177° by many recrystallisations.

Aqueous sodium carbonate does not dissolve this substance, but the solution in aqueous sodium hydroxide is yellow and, on boiling, ammonia is evolved; the orange-yellow solution must then contain dinitrohydroxyphenylpropionic acid.

Boiling with nitric acid did not change this very stable substance, and it was also unaffected by bromine in hot acetic acid solution. The demeanour of dinitrohydrocarbostyryl towards alkalis

suggests that the acidic hydroxyl of dinitrostrychol is that in the  $\beta$ -position.

*O-Methyldinitrostrychol*.—This monomethyl ether has been obtained by the variation of Tafel's procedure (*Annalen*, 1898, **301**, 345) described in Part IX (*loc. cit.*), and also in good yield by methylation with methyl sulphate and potassium hydroxide in methyl-alcoholic solution, but the most convenient method is by direct esterification with boiling 8% methyl-alcoholic sulphuric acid, the yield being quantitative. The derivative crystallised from the hot solution, and, after recrystallisation from xylene, had m. p. 195—196°.

Attempts to prepare a dimethyldinitrostrychol have been fruitless.

*Dinitrohydrazinodeoxystrychol* (VII).—Hydrazine hydrate (20 c.c. of 95%) was added to a suspension of *O*-methyldinitrostrychol (5 g.) in boiling methyl alcohol (250 c.c.). The methyl ether rapidly passed into the orange solution, but, before this process was completed, a new substance separated in voluminous yellow needles. The mixture was boiled for 10 minutes and filtered hot; the yellow crystalline residue (2.9 g.) had m. p. 202—204° (decomp.) (Found in material dried at 120° in a vacuum over phosphoric oxide: C, 41.1; H, 2.7; N, 21.3; MeO, 9.5%). This substance is a base exhibiting the reactions of a hydrazine, but the analyses, which have been confirmed, do not fit a simple formula.

The filtrate deposited a sandy, orange, crystalline powder (2.3 g.) which could be recrystallised by solution in warm acetic acid and addition of water; the pale yellow needles had m. p. 253° (decomp.) (Found in air-dried material from two different preparations: C, 38.5, 38.4; H, 3.1, 3.1; N, 25.0, 25.1; MeO, trace.  $C_9H_7O_5N_5 \cdot H_2O$  requires C, 38.2; H, 3.2; N, 24.7%). This *hydrazine* is very sparingly soluble in most organic solvents; when covered with acetic acid, it gives a colourless acetate which dissolves on heating. The hydrochloride crystallises in colourless needles, and the sulphate, which is very sparingly soluble in dilute sulphuric acid, crystallises in pearly leaflets. Solution in 2% hydrochloric acid occurred readily on gentle heating, and, on the addition of ferric chloride, a clear solution was obtained which soon clouded with evolution of nitrogen on boiling. The precipitate was collected, crystallised from acetic acid, and identified with dinitrostrychol by its properties and m. p. (284°), undepressed by admixture with a specimen prepared from dinitrostrycholcarboxylic acid. Similarly, dinitrostrychol was obtained by addition of *N*/10-potassium permanganate to a solution in 2% hydrochloric acid, although the amount of the reagent consumed was only about 30% in excess of the quantity required to supply one oxygen atom to one molecule of the base.

These experiments gave rise to the suspicion that the substance is the hydrazine salt of dinitrostrychol, although the behaviour towards acids was not in harmony with such a view and the preparation of anhydrous derivatives disproved it.

The *acetyl* derivative separated in flocculent colourless needles from a hot solution of the base in acetic acid, to which a few drops of acetic anhydride were added. The substance was very sparingly soluble and devoid of basic properties; it had m. p. 311–313° (decomp.) (Found in material dried at 100°: C, 42.9; H, 3.2; N, 22.7.  $C_{11}H_9O_6N_5$  requires C, 43.0; H, 2.9; N, 22.8%). The *isopropylidene* derivative,  $C_9NH_3(NO_2)_2(OH) \cdot NH \cdot N : CMe_2$ , crystallised from a boiling solution of the base in acetone or when acetone was added to a hot solution in dilute hydrochloric acid: recrystallised from much acetone, it formed slender, very pale yellow, microscopic needles, m. p. 279–281° (decomp.) (Found in material dried at 100°: C, 47.3; H, 3.5; N, 22.8.  $C_{12}H_{11}O_5N_5$  requires C, 47.2; H, 3.6; N, 23.0%). This very sparingly soluble derivative is insoluble in boiling dilute hydrochloric acid, but, when suspended in boiling acetone, it dissolves immediately on the addition of a drop of concentrated hydrochloric acid.

*Isolation of 3:5-Dinitrobenzoic Acid from the Products of the Oxidation of Strychnine by Means of Nitric Acid.*—Strychnine (100 g.) was dissolved in 20% nitric acid (4000 c.c.) and heated on the steam-bath for 120 hours, the volume being maintained by addition of 20% nitric acid as found necessary. The liquid was then concentrated to about 200 c.c., cooled, and kept for 36 hours. The solid was collected and washed with nitric acid; it then afforded, after boiling with nitric acid (75 c.c.,  $d$  1.42), about 10 g. of dinitrostrycholcarboxylic acid of m. p. 295–300°. The filtrate was added to water (1500 c.c.); a red gum was then deposited and a yellow solid remained in suspension. This was extracted with ether: the residue obtained from the washed and dried extract was an orange gum (about 10 g.), which was carefully heated on the steam-bath with nitric acid (90 c.c.,  $d$  1.42) and water (60 c.c.). The cooled solution deposited some picric acid, the filtrate from which was concentrated to half its volume; the glistening plates which then separated were recrystallised from alcohol. This product (3–4 g.) was analysed and, although the results showed it to be a mixture, a clue to its nature was obtained. A wasteful crystallisation from ethyl acetate gave the pure substance in colourless needles, m. p. 204°, alone or mixed with a specimen of 3:5-dinitrobenzoic acid.

Addition of aqueous sodium hydroxide to a solution of this acid



in acetone produces an intense pure blue coloration, which becomes reddish-violet on the addition of water.

The authors wish to thank Mr. F. Hall for assistance in connexion with the analyses.

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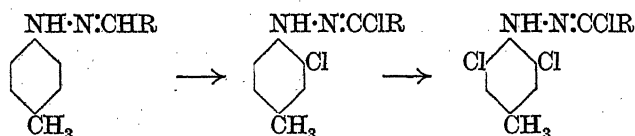
### CXI.—*Intramolecular Rearrangement in the Isomeric Tetrachloro-derivatives of p-Tolylhydrazones.*

By FREDERICK DANIEL CHATTAWAY and ARTHUR B. ADAMSON.

THE chlorination of the *p*-tolylhydrazones of *m*- and *p*-nitrobenzaldehyde at the ordinary temperature yields a series of compounds closely resembling the corresponding bromo-compounds.

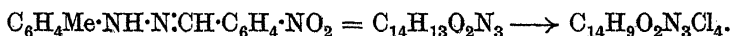
The least halogenated products that can be isolated contain two atoms of chlorine, one in the *p*-tolyl nucleus in an *o*-position with respect to the nitrogen atom and a second in the  $\omega$ -position. The same compounds are obtained by careful chlorination of the corresponding hydrazones of 3-chloro-*p*-tolylhydrazine.

Further chlorination at the ordinary temperature introduces a third atom of chlorine into the remaining *o*-position in the *p*-tolyl nucleus :



These compounds have the usual properties of  $\omega$ -halogenated compounds. On boiling with sodium acetate and acetic acid they are converted into the corresponding  $\beta$ -acetyl-hydrazides of *m*- or *p*-nitrobenzoic acid, and they are converted into the corresponding hydrazidines by the action of concentrated aqueous ammonia.

On brominating *m*- or *p*-nitrobenzaldehyde-*p*-tolylhydrazone, only three atoms of bromine can be introduced into the molecule even when a large excess of halogen is used and the temperature allowed to rise (this vol., p. 157). When, however, an acetic acid suspension of either of these hydrazones is saturated with chlorine and the temperature allowed to rise, the resulting compound contains four atoms of chlorine in the molecule :



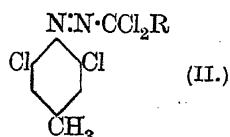
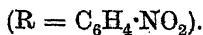
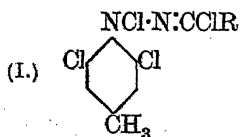
These tetrachloro- compounds are not affected by acetic anhydride and indeed can be recovered unchanged after boiling for several hours with acetic anhydride and a drop of concentrated sulphuric acid. They do not react with hot alcoholic ammonia. They liberate iodine from a solution of potassium iodide in dilute acetic acid. When treated with phenylhydrazine, they do not yield formazyl derivatives but undergo reduction to  $\omega$ -chloro-*m*- or -*p*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone : mild reduction with tin and cold hydrochloric acid also yields the same compound.

The fourth atom of chlorine cannot therefore have entered either the *p*-tolyl or the nitrobenzaldehyde nucleus.

On heating with acetic acid slightly diluted with water, they undergo a curious, exothermic, intramolecular change, considerable heat being evolved, since the mixture maintains itself at the boiling point for several minutes without external heating.

The new compounds thus formed have the same composition and molecular weight as those from which they are produced, but are much less soluble in all solvents and have much higher melting points. They have also a lighter colour, being pale yellow whilst the parent substances are deep orange, and are very unreactive. They do not react with hot alcoholic ammonia or boiling acetic anhydride, nor do they yield  $\omega$ -chloro-*m*- or -*p*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone when treated with phenylhydrazine or on mild reduction. Vigorous reduction with tin and hydrochloric acid completely breaks down the molecule and yields in each case 3 : 5-dichloro-*p*-toluidine. Boiling with acetic acid and sodium acetate gives white viscid solids which cannot be crystallised but on hydrolysis yield *m*- or *p*-nitrobenzoic acid. As in the case of the parent substances, therefore, the fourth atom of chlorine in the transformation products cannot be substituted in either the *p*-tolyl or the nitrobenzaldehyde nucleus.

It seems therefore probable that the structure of these isomerides may be best represented as  $\omega$ -chloro-*m*- or -*p*-nitrobenzaldehyde-3 : 5 : N-trichloro-*p*-tolylhydrazone (I) and 3 : 5-dichloro-*p*-tolueneazo-*m*- or -*p*-nitrophenyldichloromethane (II) :



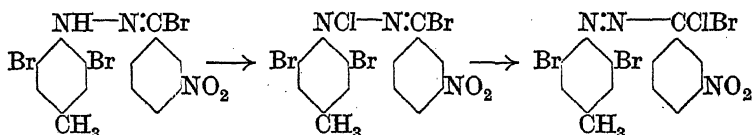
Certain facts, however, are difficult to reconcile with this supposition. For example, one would expect the compound containing the azo-linkage to have the deeper colour, whereas it is pale yellow. Also one would expect the CCl<sub>2</sub> group to be reactive and easily

hydrolysed, but it is remarkably stable and is not affected by boiling with concentrated hydrochloric acid or alcoholic ammonia.

The action of chlorine upon  $\omega$ -bromo-*m*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone yields a similar compound,



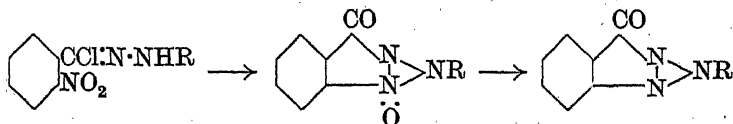
This also is converted into an isomeride of higher melting point by boiling with acetic acid slightly diluted with water :



Corresponding compounds are not produced under similar conditions by the action of chlorine upon *m*- and *p*-nitrobenzaldehyde-phenylhydrazone, the highest chlorination product being  $\omega$ -chloro-*m*- or -*p*-nitrobenzaldehyde-2 : 4 : 6-trichlorophenylhydrazone.

The chlorination of *o*-nitrobenzaldehyde-*p*-tolylhydrazone follows a normal course. The first product which can be isolated is  $\omega$ -chloro-*o*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone. Saturation with chlorine at the ordinary temperature yields  $\omega$ -chloro-*o*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone.

These two  $\omega$ -chloro-compounds are rather more stable than the corresponding bromo-compounds and can be recrystallised unchanged from alcohol. They readily yield the corresponding *ketoendoaryliminodihydrobenzisodiazole oxides*, which are violently explosive, when a little concentrated aqueous ammonia is added to their solution in benzene. On mild reduction, these explosive compounds lose one atom of oxygen and are converted into the corresponding *ketoendoaryliminodihydrobenzisodiazoles* :



If the temperature is allowed to rise during the chlorination of *o*-nitrobenzaldehyde-*p*-tolylhydrazone, the hydrazone is rapidly decomposed and consequently a higher chlorination product such as is formed in the case of *m*- and *p*-nitrobenzaldehyde-*p*-tolylhydrazone cannot be obtained.

#### EXPERIMENTAL.

##### *The Chlorination of m-Nitrobenzaldehyde-p-tolylhydrazone.*

$\omega$ -Chloro-*m*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone.—Chlorine was slowly passed into a suspension of 5 g. of *m*-nitro-

benzaldehyde-*p*-tolylhydrazone in 50 c.c. of acetic acid. The hydrazone dissolved and almost immediately  $\omega$ -chloro-*m*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone began to separate as a bright yellow solid. When the mixture had become almost solid, chlorination was stopped and the solid collected. It crystallised from acetic acid, in which it was moderately easily soluble, in bright yellow, elongated plates, m. p. 137° (Found : Cl, 29.6.  $C_{14}H_{10}O_2N_3Cl_3$  requires Cl, 29.7%).

*m*-Nitrobenz- $\beta$ -acetyl-3 : 5-dichloro-*p*-tolylhydrazide,



—2 G. of  $\omega$ -chloro-*m*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone, 2 g. of anhydrous sodium acetate, and 40 c.c. of acetic acid were boiled under reflux for 2 hours. The resulting solution was poured into 100 c.c. of cold water. The hydrazide, which separated as a white solid, crystallised from alcohol, in which it was moderately easily soluble, in small prisms, m. p. 173° (Found : Cl, 18.5.  $C_{16}H_{13}O_4N_3Cl_2$  requires Cl, 18.6%).

A lower chlorination product of *m*-nitrobenzaldehyde-*p*-tolylhydrazone could not be isolated in a pure state.

$\omega$ -Chloro-*m*-nitrobenzaldehyde-3 : 5 : *N*-trichloro-*p*-tolylhydrazone (I).

—A suspension of 5 g. of *m*-nitrobenzaldehyde-*p*-tolylhydrazone in 50 c.c. of acetic acid was saturated with chlorine, the temperature being allowed to rise to about 60°. The bright yellow  $\omega$ -chloro-*m*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone first separated, but this slowly redissolved, forming an orange solution. From this, on standing for 12 hours at the ordinary temperature,  $\omega$ -chloro-*m*-nitrobenzaldehyde-3 : 5 : *N*-trichloro-*p*-tolylhydrazone slowly separated. After being washed with a very little acetic acid, this crystallised from alcohol, in which it was easily soluble, in orange four-sided prisms, m. p. 95° (Found : C, 43.1; H, 2.3; N, 10.7; Cl, 36.3; *M*, cryoscopic in benzene, 375.  $C_{14}H_9O_2N_3Cl_4$  requires C, 42.8; H, 2.3; N, 10.7; Cl, 36.1%; *M*, 393).

*Action of Phenylhydrazine on  $\omega$ -Chloro-*m*-nitrobenzaldehyde-3 : 5 : *N*-trichloro-*p*-tolylhydrazone.*—2 G. of phenylhydrazine were added to a solution of 2 g. of the hydrazone in 20 c.c. of acetic acid and warmed until a brisk reaction started. The solution became dark brown and on cooling,  $\omega$ -chloro-*m*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone separated, m. p. 137° after several crystallisations from acetic acid.

*Reduction of  $\omega$ -Chloro-*m*-nitrobenzaldehyde-3 : 5 : *N*-trichloro-*p*-tolylhydrazone.*—4 G. of the hydrazone were dissolved in 30 c.c. of acetic acid, 15 c.c. of hydrochloric acid and 3 g. of granulated tin were added, and the mixture was warmed gently for a few minutes.  $\omega$ -Chloro-*m*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone separ-

ated as an oil which quickly solidified; m. p. 137° after crystallisation from acetic acid.

*Intramolecular Rearrangement of  $\omega$ -Chloro-m-nitrobenzaldehyde-3 : 5 : N-trichloro-p-tolylhydrazone (I) into 3 : 5-Dichloro-p-tolueneazo-m-nitrophenyldichloromethane (II).*—5 G. of the hydrazone were dissolved in 100 c.c. of hot acetic acid, 5 c.c. of water added, and the solution raised to the boiling point. A brisk reaction took place, the mixture continued boiling for several minutes without external heating, and 3 : 5-dichloro-p-tolueneazo-m-nitrophenyldichloromethane separated as a pale yellow solid. The mixture was heated until there was no further separation of solid. After cooling, the product was collected and washed with alcohol, in which it was practically insoluble; it crystallised from acetic acid, in which it was moderately easily soluble, in pale yellow needles, m. p. 165° (Found : C, 43.0; H, 2.4; N, 10.6; Cl, 35.9; *M*, ebullioscopic in benzene, 388.  $C_{14}H_9O_2N_3Cl_4$  requires C, 42.8; H, 2.3; N, 10.7; Cl, 36.1%; *M*, 393).

*Reduction of 3 : 5-Dichloro-p-tolueneazo-m-nitrophenyldichloromethane.*—To 5 g. of the dichloromethane, suspended in a mixture of 50 c.c. of acetic acid and 50 c.c. of hydrochloric acid, 5 g. of granulated tin were added and the mixture was heated until a clear, almost colourless solution was formed. This was cooled, made alkaline with caustic soda, and steam-distilled. 3 : 5-Dichloro-p-toluidine separated in the distillate as a white solid and was identified by means of its acetyl derivative, which crystallised from alcohol in colourless prisms, m. p. 207°, identical with a specimen prepared by the chlorination of aceto-p-toluidide.

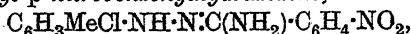
*Reaction of 3 : 5-Dichloro-p-tolueneazo-m-nitrophenyldichloromethane with Sodium Acetate and Acetic Acid.*—A mixture of 3 g. of the dichloromethane, 3 g. of anhydrous sodium acetate, and 60 c.c. of acetic acid was boiled under reflux for 2 hours. The clear solution obtained was cooled and poured into 200 c.c. of cold water; a colourless semi-solid mass then separated which could not be made to crystallise. It was therefore boiled under reflux with a mixture of 25 c.c. of alcohol and 25 c.c. of hydrochloric acid for 2 hours; the solution obtained was cooled and made alkaline, and the alcohol distilled off. After filtration from tarry matter, the colourless liquid was acidified with hydrochloric acid; ether then extracted *m*-nitrobenzoic acid, m. p. 140° after crystallisation from water.

#### *The Chlorination of p-Nitrobenzaldehyde-p-tolylhydrazone.*

*$\omega$ -Chloro-p-nitrobenzaldehyde-3-chloro-p-tolylhydrazone.*—A very slow stream of chlorine was passed into a solution of 2 g. of *p*-nitrobenzaldehyde-p-tolylhydrazone in 150 c.c. of acetic acid, cooled in

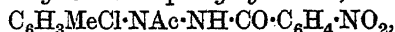
running water. In a few minutes  $\omega$ -chloro-*p*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone separated as an orange flocculent solid. Chlorination was then stopped. The product, after being washed with water, crystallised from acetic acid, in which it was moderately easily soluble, as a felted mass of slender, bright orange prisms, m. p. 163° (Found: Cl, 21.9.  $C_{14}H_{11}O_2N_3Cl_2$  requires Cl, 21.9%).

3-Chloro-*p*-tolyl-*p*-nitrobenzenylhydrazidine,



which separated when a suspension of 2 g. of  $\omega$ -chloro-*p*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone in 20 c.c. of alcohol was heated with 2 c.c. of concentrated aqueous ammonia, until a clear dark purple solution was formed, and then cooled, crystallised from alcohol, in which it was moderately easily soluble, in deep purple prisms, m. p. 162° (Found: Cl, 11.8.  $C_{14}H_{13}O_2N_4Cl$  requires Cl, 11.7%).

*p*-Nitrobenz- $\beta$ -acetyl-3-chloro-*p*-tolylhydrazide,



separated as a white solid when the solution obtained by boiling 2 g. of  $\omega$ -chloro-*p*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone, 2 g. of anhydrous sodium acetate, and 40 c.c. of acetic acid under reflux for 2 hours was poured into 100 c.c. of cold water. It crystallised from alcohol, in which it was moderately easily soluble, in small colourless prisms, m. p. 164° (Found: Cl, 10.2.  $C_{16}H_{14}O_4N_3Cl$  requires Cl, 10.2%).

$\omega$ -Chloro-*p*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone.—This was obtained, in the same way as the *m*-nitro-compound, from 4 g. of *p*-nitrobenzaldehyde-*p*-tolylhydrazone in 100 c.c. of acetic acid; the intermediately formed 3-chloro-*p*-tolylhydrazone separated but quickly redissolved. The 3 : 5-dichloro-*p*-tolylhydrazone crystallised from acetic acid, in which it was moderately easily soluble, in slender, bright yellow prisms, m. p. 139° (Found: Cl, 29.6.  $C_{14}H_{10}O_2N_3Cl_3$  requires Cl, 29.7%).

3 : 5-Dichloro-*p*-tolyl-*p*-nitrobenzenylhydrazidine crystallises from alcohol in orange-yellow plates, m. p. 159° (Found: Cl, 21.2.  $C_{14}H_{12}O_2N_4Cl_2$  requires Cl, 21.2%).

*p*-Nitrobenz- $\beta$ -acetyl-3 : 5-dichloro-*p*-tolylhydrazide crystallises from alcohol in small colourless prisms, m. p. 183° (Found: Cl, 18.8.  $C_{16}H_{13}O_4N_3Cl_2$  requires Cl, 18.6%).

$\omega$ -Chloro-*p*-nitrobenzaldehyde-3 : 5 : N-trichloro-*p*-tolylhydrazone, obtained, in the same way as the *m*-nitro-compound, from 10 g. of *p*-nitrobenzaldehyde-*p*-tolylhydrazone in 70 c.c. of acetic acid, crystallised from acetic acid, in which it was easily soluble, in irregular orange plates, m. p. 97° (Found: C, 42.3; H, 2.6; N, 10.9; Cl, 35.9; *M*, cryoscopic in benzene, 383.  $C_{14}H_9O_2N_3Cl_4$  requires C, 42.8; H, 2.3; N, 10.7; Cl, 36.1%; *M*, 393).

This compound was treated in the manner described under  $\omega$ -chloro-*m*-nitrobenzaldehyde-3 : 5 : N-trichloro-*p*-tolylhydrazone and its behaviour was exactly similar. It gave  $\omega$ -chloro-*p*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone, m. p. 139°, on treatment with phenylhydrazine or on reduction with tin and hydrochloric acid and was converted by boiling dilute acetic acid into 3 : 5-dichloro-*p*-tolueneazo-*p*-nitrophenyldichloromethane, which crystallised from acetic acid, in which it was moderately easily soluble, in bright yellow, elongated plates, m. p. 188° (Found : C, 43.1; H, 2.4; N, 10.9; Cl, 35.8; *M*, ebullioscopic in benzene, 410.  $C_{14}H_9O_2N_3Cl_4$  requires C, 42.8; H, 2.3; N, 10.7; Cl, 36.1%; *M*, 393).

The azo-compound gave 3 : 5-dichloro-*p*-toluidine (acetyl-derivative, m. p. 207°) on reduction with tin and hydrochloric acid and was converted by boiling acetic acid and anhydrous sodium acetate into a white viscid solid, which gave *p*-nitrobenzoic acid, m. p. 238°, on hydrolysis.

*The Chlorination of  $\omega$ -Bromo-*m*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone.*

$\omega$ -Bromo-*m*-nitrobenzaldehyde-N-chloro-3 : 5-dibromo-*p*-tolylhydrazone.—A rapid stream of chlorine was passed into a suspension of 5 g. of  $\omega$ -bromo-*m*-nitrobenzaldehyde-3 : 5-dibromo-*p*-tolylhydrazone in 50 c.c. of hot acetic acid. From the orange solution produced, on cooling,  $\omega$ -bromo-*m*-nitrobenzaldehyde-N-chloro-3 : 5-dibromo-*p*-tolylhydrazone slowly separated. This crystallised from alcohol, in which it was easily soluble, in deep orange prisms, m. p. 77° (Found : C, 32.0; H, 1.7; N, 8.1; Cl + Br, 52.8.  $C_{14}H_9O_2N_3ClBr_3$  requires C, 31.9; H, 1.7; N, 8.0; Cl + Br, 52.3%).

By the method used in the two previous rearrangements, the chlorodibromotolylhydrazone was converted into 3 : 5-dibromo-*p*-tolueneazo-*m*-nitrophenylchlorobromomethane, which crystallised from acetic acid, in which it was moderately easily soluble, in pale yellow needles, m. p. 157° (Found : C, 32.1; H, 1.8; N, 7.9; Cl + Br, 52.3.  $C_{14}H_9O_2N_3ClBr_3$  requires C, 31.9; H, 1.7; N, 8.0; Cl + Br, 52.3%).

*The Chlorination of o-Nitrobenzaldehyde-p-tolylhydrazone.*

$\omega$ -Chloro-*o*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone.—A slow stream of chlorine was passed into a suspension of 5 g. of *o*-nitrobenzaldehyde-*p*-tolylhydrazone in 25 c.c. of acetic acid until the hydrazone just dissolved, forming a dark brown solution. From this,  $\omega$ -chloro-*o*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone slowly separated. It crystallised from alcohol, in which it was easily

soluble, in orange rhombic plates, m. p.  $103^{\circ}$  (Found: Cl, 21.7.  $C_{14}H_{11}O_2N_3Cl_2$  requires Cl, 21.9%).

*3-Keto-1 : 2-endo-3'-chloro-p-tolylimino-2 : 3-dihydro-1 : 2-benzisodiazole 1-Oxide*.—This separated as a bright yellow solid when a solution of  $\omega$ -chloro-*o*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone (3 g.) in benzene was warmed with 3 c.c. of concentrated aqueous ammonia. It crystallised from alcohol, in which it was moderately easily soluble, in bright yellow, rhombic plates, explosion point  $134^{\circ}$  (Found: Cl, 12.1.  $C_{14}H_{10}O_2N_3Cl$  requires Cl, 12.3%).

*3-Keto-1 : 2-endo-3'-chloro-p-tolylimino-2 : 3-dihydro-1 : 2-benzisodiazole*.—A solution of stannous chloride (2 g.) in hydrochloric acid was added to a solution of the explosive compound (2 g.) in 5 c.c. of acetic acid and 5 c.c. of hydrochloric acid. On dilution with water, the product separated as a pale yellow solid. It crystallised from alcohol, in which it was easily soluble, in colourless needles, m. p.  $173^{\circ}$  (Found: Cl, 13.2.  $C_{14}H_{10}ON_3Cl$  requires Cl, 13.1%).

*$\omega$ -Chloro-*o*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone*.—A suspension of 5 g. of *o*-nitrobenzaldehyde-*p*-tolylhydrazone in 25 c.c. of acetic acid, cooled to the ordinary temperature in running water, was saturated with chlorine. The hydrazone dissolved and a deep yellow solution was finally obtained, from which  *$\omega$ -chloro-*o*-nitrobenzaldehyde-3 : 5-dichloro-*p*-tolylhydrazone* slowly separated. It crystallised from alcohol, in which it was easily soluble, in pale yellow, six-sided plates, m. p.  $87^{\circ}$  (Found: Cl, 29.8.  $C_{14}H_{10}O_2N_3Cl_3$  requires Cl, 29.7%).

*3-Keto-1 : 2-endo-3' : 5'-dichloro-*p*-tolylimino-2 : 3-dihydro-1 : 2-benzisodiazole 1-oxide*, obtained in a similar way to the preceding oxide, crystallised from alcohol, in which it was moderately easily soluble, in bright yellow, six-sided plates, explosion point  $155^{\circ}$  (Found: Cl, 21.9.  $C_{14}H_9O_2N_3Cl_2$  requires Cl, 22.0%). On reduction with stannous chloride it gave *3-keto-1 : 2-endo-3' : 5'-dichloro-*p*-tolylimino-2 : 3-dihydro-1 : 2-benzisodiazole*, which crystallised from alcohol, in which it was easily soluble, in colourless six-sided prisms, m. p.  $202^{\circ}$  (Found: Cl, 22.9.  $C_{14}H_9ON_3Cl_2$  requires Cl, 23.2%).

THE QUEEN'S COLLEGE LABORATORY,  
OXFORD.

[Received, January 29th, 1930.]



# ANNUAL GENERAL MEETING,

THURSDAY, MARCH 27TH, 1929, AT 4 P.M.

THE President, Professor J. F. THORPE, C.B.E., D.Sc., F.R.S., was in the Chair.

The Report of the Council for 1929—1930, together with the Balance Sheets and Statements of Accounts for 1929, was presented by the PRESIDENT, and the TREASURER made a statement regarding the finances of the Society. The adoption of the Report and Accounts, proposed by Dr. J. A. VOELCKER and seconded by Professor J. KENNER, was carried unanimously.

## REPORT OF COUNCIL, 1929—1930.

### *I. Fellowship Statistics.*

THE number of Fellows at the 31st December, 1928, was 3980. During 1929, 210 Fellows were elected and 8 reinstated, as against 203 and 11 in 1928, giving a gross total of 4198. Deaths of 49 Fellows were recorded, 107 resigned, and the names of 117 were removed from the List of Fellows for non-payment of Annual Subscriptions, the corresponding figures for last year being 40, 135, and 99, respectively. The total number of Fellows at the 31st December, 1929, was 3925, showing a decrease of 55, as against 60 the previous year.

The Council records with sorrow the death on the 17th September of a distinguished Fellow of the Society, Professor W. H. Perkin, who served as President from 1913 to 1915 and on the Council for a total of twenty years. At its meeting on the 17th October, the Council passed a special resolution of sympathy, which was read at the Ordinary Scientific Meeting and conveyed to Mrs. Perkin by the President, who, together with the Secretaries and other Members of Council, represented the Society at the funeral. A comprehensive account of the life and work of Professor Perkin is being prepared by Mr. A. J. Greenaway, Professor R. Robinson, and Professor J. F. Thorpe, and will be published in the Journal.

The Society has also to mourn the loss of two of its Honorary Fellows, Professor Charles Moureu, elected on the 1st March, 1923, who was the first President of the Union Internationale de Chimie and a former President of the Société Chimique de France, and Dr. T. B. Osborne, who was elected on the 7th March, 1912. An obituary notice of Dr. Osborne appeared in the Journal for 1929, p. 2974, and Sir William J. Pope is preparing an obituary notice of Professor Moureu.

During 1929, 11 Honorary Fellows were elected, the total number at the end of the year being 31.

## II. *Jubilee Fellows.*

The congratulations of the Society have been sent to the following Fellows who have attained their Jubilee as Fellows :

	Elected.
William Thomas Gent .....	April 17th, 1879.
William Stone .....	April 17th, 1879.
Alfred Walter Stokes .....	April 17th, 1879.
Charles Slater .....	April 17th, 1879.
Frank Litherland Teed .....	April 17th, 1879.
Victor Herbert Veley .....	April 17th, 1879.
George Richard Tweedie .....	June 19th, 1879.
Joji Sakurai .....	June 19th, 1879.
George Stacey Albright .....	December 18th, 1879.
Wyndham Rowland Dunstan .....	December 18th, 1879.
Joshua Knowles .....	December 18th, 1879.
Henry Forster Morley .....	December 18th, 1879.
Alexander Scott .....	December 18th, 1879.
George Stallard .....	December 18th, 1879.
William Macnab .....	February 19th, 1880.
Alexander Kenneth Miller .....	February 19th, 1880.

## III. *Journal.*

The Journal for 1929 contains 2981 pages, of which 2899 pages are occupied by 400 memoirs and 31 notes, the remaining 82 pages being devoted to Obituary Notices (13 pages), two Lectures (29 pages), the Report of the Annual General Meeting (17 pages), the Presidential Address (19 pages), and Table of Atomic Weights (4 pages). The volume for 1928 contains 438 memoirs and 28 notes, occupying 3216 pages.

During 1929, 466 papers were offered to the Society for publication in the Journal; of these, 21 were declined. The corresponding numbers for 1928 are 501 and 15. The average interval between the dates of receipt and of publication of papers is 9.8 weeks for 1929, and 10.75 weeks for 1928.

The Council records its sincere appreciation of the arduous and responsible work undertaken by Fellows in refereeing papers submitted for publication.

## IV. *Abstracts.*

The "A" Abstracts for 1929 contained 10,463 abstracts, occupying 1500 pages, compared with the corresponding figures for 1928 of 9456 and 1408 respectively. These comprised 5346 in General, Physical, and Inorganic Chemistry, 189 in Geochemistry, 2326 in Organic Chemistry, and 2602 in Biochemistry. The corresponding figures for 1928 were 4718, 224, 2236, and 2268.

The expansion of published chemical work, reflected in the 10 per cent. increase in the number of abstracts for 1929 as compared

with 1928, still continues. From the figures quoted in the foregoing paragraph, it will be seen that the increase has been specially marked in the sections of General, Physical, and Inorganic Chemistry and Biochemistry. The total of 10,463 "A" abstracts for 1929 may be compared also with corresponding figures for earlier years, such as 5978 (in 1913), 5572 (in 1923), and 7978 (in 1926). The number of "B" abstracts in 1929 was 9717, so that the total number of abstracts published by the Bureau in one year has now exceeded the 20,000 figure.

*Annual Index.* The Joint Annual Index for the 1928 abstracts covered 576 pages, as compared with 514 pages in the previous year. The cost of printing was £1187 16s. 10d., and the cost of paper £261 17s. 5d., representing an increase in both respects, although the cost of printing *per page* was £2 1s. 3d. in 1928, as compared with £2 4s. 2d. in 1927.

*Collective Index.* During the past year the Bureau devoted much consideration to the question of a Collective Index for the period 1923-32, and the relevant facts and figures were submitted to the two Councils concerned. With the sanction and substantial financial support of both bodies, and with the further aid of a grant promised by the Royal Society, the Bureau expects to proceed with the preparation of the Index, as soon as it appears that adequate support from subscribers is forthcoming.

#### V. Library.

Excluding the evenings on which meetings of the Chemical Society were held, there were 7567 attendances during the past year as compared with 8037 in 1928. Of the 7567, 4962 were made by Fellows of the Chemical Society, while 2605 were made by Members of Contributing Societies, as against 2669 in 1928.

The number of books borrowed during 1929 was 5402, as against 5262 the previous year; of these 1466 were issued by post, as against 1337 in the preceding year.

The additions to the Library comprise: 231 books, of which 71 were presented, 690 volumes of periodicals and 150 pamphlets; as against 281 books, 664 volumes of periodicals and 138 pamphlets last year. The total number of volumes added during the year was 921, showing a decrease of 24. The Library now contains 33,753 volumes, consisting of 10,159 books and 23,594 bound volumes of periodicals.

#### VI. General.

*Lectures.* The first Pedler Lecture, entitled "The Early History of the Synthesis of Closed Carbon Chains," was delivered by Professor

W. H. Perkin on the 30th May, and has been published in the Journal for 1929 (p. 1347). The second Liversidge Lecture, given by Professor H. Freundlich on the 12th December and entitled "Surface Forces and Chemical Equilibria," has also been published in the Journal (1930, p. 164).

On the 25th April Sir Harold Hartley delivered a Memorial Lecture on the Life and Work of the late Theodore W. Richards, which will be published during 1930.

The Council has conveyed its thanks to these lecturers.

Professor G. von Hevesy and Professor Niels Bohr have accepted the invitation of Council to be the Hugo Müller and Faraday Lecturers respectively in 1930.

*Anniversary Meeting.* The Annual General Meeting was held at the University of Leeds on the 21st March, and the Anniversary Dinner, at which the chief guests were the Viscount Lascelles, K.G. (the present Earl of Harewood), the Vice-Chancellor of the University, and the Lord Mayor of Leeds, was held the same evening in the Town Hall. The large attendance at these functions has confirmed the Council in its view that there is a general desire on the part of the Fellows that Annual Meetings should be held in the Provinces at frequent intervals. An account of the Annual General Meeting appears in the Journal, p. 817, and a report of the Dinner in the Proceedings (p. 37).

*Representatives at Celebrations and on Committees.* The President, accompanied by the Senior Secretary, represented the Society at the Paul Schutzenberger Centenary Celebrations in Paris on the 7th November, 1929, and presented an address of congratulation. The President also represented the Society at the opening of the Imperial Chemical Industries' Agricultural Station at Maidenhead.

Principal R. H. Raikes represented the Society at the Centenary Celebrations of the South African College at Cape Town, and presented the Society's congratulatory Address. The Prince Ginori Conti was the Society's delegate at the III<sup>ème</sup> Congrès National de Chimie Pure et Appliquée at Florence, and the Society was represented by Mr. R. Truszkowski at the II<sup>ème</sup> Congrès des Chimistes Polonais at Poznan, by Dr. L. H. Lampitt at the IX<sup>ème</sup> Congrès de Chimie Industrielle at Barcelona, and by Dr. K. Fisher at the Conference on Educational Films in London.

Professor C. S. Gibson, Mr. A. J. Greenaway, Dr. J. T. Hewitt, Professor G. T. Morgan, and the Treasurer have continued to be the Society's members of the Bureau of Chemical Abstracts, and the Society's representatives on the Federal Council for Chemistry are Professor C. S. Gibson, Sir William J. Pope, and Professor J. F.

Thorpe. Professor R. Whytlaw Gray has been appointed by the Council to represent the Society on the recently formed Colloid Committee of the Faraday Society, and Professor W. A. Bone represented the Society on the Committee appointed by the Association of British Chemical Manufacturers to consider amendments in the Patents and Designs Acts (see p. 856).

*Liebig Portrait.* The copy of the "Muspratt" portrait of Liebig, which, as stated in the last Report of Council, had been painted by Mr. G. A. Pownall, was presented on behalf of the Society to the German Chemical Society on the 8th May by the President, when he and the Senior Secretary attended a special meeting in Berlin.

*Longstaff Medal.* The Longstaff Medal for 1930 has been awarded to Dr. W. H. Mills for his distinguished researches in organic chemistry especially in relation to stereochemistry. The presentation will be made at the Annual General Meeting on the 27th March.

*Fellowship Statistics.* The statistics given at the beginning of this report show that the diminution in the number of Fellows referred to in the last report still persists, and the matter is being carefully considered by the Council, which has appointed a Committee to enquire into the matter. This Committee has presented an *interim* report which, in particular, draws attention to the fact that a falling-off in membership concerns also the Society of Chemical Industry, and that close co-operation between the two societies may be desirable in any steps which may be taken to remedy this state of affairs. The matter is still under consideration and an announcement will be made in due course.

The action of the Council in approaching Chemical Societies abroad with a view to the mutual publication of terms of membership has met with a cordial response, and particulars received by the Society from the Deutsche Chemische Gesellschaft, the Norsk Kjemisk Selskap, the Real Sociedad Española de Física y Química, and the Suomalaisten Kemistien Seura were included at the end of the Journal for January, 1930.

*A Central Building in London for Scientific and Technical Institutions.* There would appear to be little need to remind Fellows of the urgent necessity for larger and more convenient accommodation for the Society, which has occupied its present apartments since 1874, when the number of Fellows was 733. In May, the President informed the Council that he had been approached with respect to

the possibility of the Chemical Society co-operating in a scheme for providing in London a Central Building for housing certain scientific and technical institutions. A Committee was appointed to enquire into and report upon the scheme, and in June the Council, on the recommendation of this Committee, agreed to the principle involved. The President (or in his absence, the Senior Secretary) was appointed to serve on the General Exploring Committee, and the President, Professor C. S. Gibson, and Dr. F. L. Pyman were elected to serve on a Joint Chemical Committee composed of representatives appointed by the Chemical Society, the Society of Chemical Industry, the Institution of Chemical Engineers, and the Institution of the Rubber Industry. This Joint Committee has met on several occasions, and the Council hopes shortly to be in a position to make an important announcement indicating the progress that has been made.

*Presidency.* In view of the important part which the President of the Society must take in the furtherance of the scheme, and in order that continuity of effort may be maintained, the Council has nominated the retiring President for another term of office. Professor Thorpe has accepted nomination on the understanding that he is at liberty to place his resignation in the hands of the Council at the end of the first year of the new period of office.

*Patents and Designs Acts.* In the Proceedings for June, the Council directed the attention of Fellows to the arrangements made by the Federal Council for Chemistry in connection with the preparation of a joint memorandum representing the considered views of chemists as to whether any, and if so what, amendments in the Patents and Designs Acts, or changes in the practice of the Patent Office, were desirable. Fellows were invited to send suggestions for consideration by the Committee of the Association of British Chemical Manufacturers, which was also acting as the Committee of the Federal Council for Chemistry. The Council is informed that the memorandum has now been presented to the Board of Trade.

*Nomenclature.* The Council has received from the Bureau of the Union Internationale de Chimie a request to publish in the Journal the proposed reforms in the Nomenclature of Organic and Inorganic Chemistry adopted by the Council of the Union Internationale. The matter was referred to the Federal Council for Chemistry and, at its suggestion, the Secretaries wrote informing the Bureau of the Union that the Federal Council, representing the opinion of British chemists, considered that publication of these reports should be postponed until they had been further considered by Committees on which the opinion of all adherents to the Union was represented.

*Atomic Constants.* The Council has directed the attention of the Federal Council for Chemistry to the desirability of the regular publication of International Tables of Atomic Constants.

The *List of Fellows*, published this year by the direction of the Council, was issued in October. This list, in addition to the usual information, indicates the various Constituent Organisations of the Federal Council for Chemistry of which Fellows are members.

*Journal of Physical Chemistry.* The Council was informed in October that the Chemical Foundation had agreed to be responsible for the business arrangements of the *Journal of Physical Chemistry*. Professor A. J. Allmand and Professor F. G. Donnan have been appointed by the Council to represent the Society on the British Editorial Board for a further period of two years.

*Annual Reports.* The volume of Annual Reports for 1929 includes, in addition to the usual subjects, a report on Crystallography and a biennial report on Mineralogical Chemistry.

The Council desires to thank those who have contributed to this volume.

*Research Fund.* Applications for research grants received during the year amounted to £901 and the sum allotted was £736 (Proceedings, pp. 74 and 123).

*Bequest and Gifts.* The Council has received intimation that under the will of the late Professor W. H. Perkin the sum of £1000 subject to a life interest has been bequeathed to the Publications Fund of the Society. It has also gratefully accepted an offer to present to the Society a life-size bronze plaque of Professor Perkin from his colleagues and students. The offer was made through Professor J. F. Thorpe, Chairman of the Perkin Memorial Fund Committee.

The Proceedings for January 1930 (pp. 1 and 2) contain an account of the presentation to the Society of a Silver Mace by Mr. Ayerst Henham Hooker to commemorate his attaining his Jubilee as a Fellow. Professor Joji Sakurai, who has also recently celebrated his jubilee as a Fellow, has sent a contribution of £10 to mark the occasion (Proceedings 1929, p. 69). The Council records its particular appreciation of the generosity of these two jubilee Fellows, and has also expressed its thanks to Mr. Basil Holmes for a framed photograph (dated 1878) of a group of Fellows of the Royal Society, and to Mr. E. W. J. Neave for a set of Journals from 1921 to 1927.

The Annual Chemical Dinner, in which the Chemical Society co-operated, was held in the Connaught Rooms on the 8th November, the principal guest of the evening being the Rt. Hon. Lord Dewar.

The Chemical Club has met eleven times during the year, and now dines on the days of the meetings of Council and of special lectures at the New Lauriers Restaurant, 102, Jermyn Street, S.W. 1.

### VII. *Financial.*

*General Purposes Account.* The income of the Society for 1929 is less than that for 1928 by £94 3s. 7d. and the expenditure greater by £133 12s. 10d.

The chief reason for the decreased income is the loss of £306 17s. in the amount received as Annual Subscriptions. There is an increase of £64 13s. 7d. in income tax recovered, and of £158 11s. 9d. on deposit interest, the latter being due to the Society placing on deposit the money received on account of the sales of publications. Administration Expenses have increased by £12 19s. 9d. The sum paid as salaries is £93 18s. 4d. in excess of that for last year; in this is included a bonus of £55 granted to the staff in consideration of the extra work involved in the Society acting as its own publisher. It has also been necessary to engage an extra junior clerk. Furniture, House Expenses, and Repairs are less than last year by £59 2s. 1d., Miscellaneous Expenses by £39 3s. 2d., and the sum transferred to the Publications Fund Account by £723 7s. 2d. Increased expenditure was incurred of £58 3s. 2d. in Miscellaneous Printing and Stationery and of £40 10s. 5d. in Expenses of Meetings. The sum of £350 transferred to Pensions Fund Account is £200 in excess of that for last year. The contribution to the Library is £118 15s. 1d. higher than in 1928. £500 has been transferred to the Special Publication Fund Account to form a Sinking Fund which shall meet in part the cost of the preparation and publication by the Bureau of Chemical Abstracts of the Collective Index 1923-1932. The Council has further resolved that the sum of £250 shall be transferred to this fund in January of each year from 1930 to 1933 inclusive and that the Special Publications Fund shall finance the project up to an amount not exceeding £2000.

*Publications Fund Account.* Omitting from the income account the sums of £243 19s. 5d. in 1929 and £220 3s. 11d. in 1928, which have been capitalised, and the sums transferred from General Purposes Account, the income for 1929 exceeds that for 1928 by £588 6s. 6d. This is mainly due to an increase of £540 5s. 10d. in the sales of publications, which is approximately the sum paid last year as commission to the former Publishers and represents a considerable saving to the Society.

*Journal.* The total expenditure on the Journal shows a decrease of £360 1s. 3d. compared with last year. The cost of printing and



paper is down by £389 8s. 7d. owing to the number of pages being 235 less; distribution and banding are less by £52 8s. 6d. Editorial salaries have increased by £113.

*Abstracts.* Expenditure on account of the Abstracts this year shows an advance of £84 0s. 1d. over that for 1928. Printing is higher by £97 4s. 10d. owing to there being 92 more pages, and to the cost of the index being increased by £78 5s. 1d. The saving of £102 4s. 1d. in the cost of paper is due to an excess of stock having been purchased in 1928.

*List of Fellows.* The List of Fellows cost £143 14s. 9d. as against £129 8s. 2d. when it was issued in 1927.

*Library.* The contribution from the General Funds of the Society exceeds that for 1928 by £118 15s. 1d. The sum spent on books and periodicals and on binding is greater by £93 8s. 3d. and salaries are higher by £32 12s. 6d. It will be seen that approximately a quarter of the total sum expended on the Library is met by the Contributing Societies.

*Staff Pensions Fund Account.* If the sum of £9 11s. 3d. under Miscellaneous Receipts be disregarded it will be seen that the expenditure exceeds the income from investments by £92 14s. 10d. The Council decided that the sum of £350 should be transferred from General Purposes Account to meet this deficit and that the balance should be invested. The capital of the fund now stands at £907 14s. The Council desires to emphasise the need for further donations in order that the income from the Fund may be such as will enable it to meet the present charges and the further demands that in course of time will be made upon it.

*General.* A contribution of £50 has been made to the Federal Council for Chemistry for the year 1929, and a donation of £5 has been sent to the New International Association for Testing Materials.

The thanks of the Council have been conveyed to the Royal Society for the sum of £250 received from the Government Publications Grant towards the cost of the Society's publications for 1929, and to Imperial Chemical Industries, Ltd., for a contribution of £100 to the Publications Fund.

The sum of £200 on the Publications Fund Account has been invested in London Midland and Scottish Railway 4 per cent. Guaranteed Stock, and the 5 per cent. War Loan Stock 1929-1947 amounting to £11,149 11s. 10d. has been converted into 5 per cent. Conversion Loan, 1944-1964.

A vote of thanks to the Auditors, Dr. O. L. Brady, Dr. A. E. Dunstan, and Dr. P. Haas, for auditing the Accounts for 1929 was proposed by the TREASURER, seconded by Professor C. S. GIBSON, and carried, acknowledgment being made by Dr. O. L. BRADY.

It was moved from the Chair and carried that Professor J. C. Drummond, Dr. P. Haas, and Dr. J. Kenyon be elected Auditors to audit the Accounts of the Society for 1930.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, Council, and Committees for their services during the past year was proposed by Professor C. K. INGOLD and seconded by Mr. E. HINKS. Acknowledgment was made by Professor F. G. DONNAN.

In presenting the Longstaff Medal for 1930 to Dr. W. H. Mills, F.R.S., the PRESIDENT said :—

“Dr. Mills, it is my pleasant duty to present to you the Longstaff Medal which has been unanimously awarded to you by the Council.

“The Medal was established by a resolution of Council dated December 21st, 1876, by which it was agreed to accept a donation of £1000 to the Research Fund by Dr. Longstaff on the understanding that ‘a gold medal of not less value than £20 be awarded triennially to the Fellow of the Society who, in the opinion of Council, has done the most to promote Chemical Science by research.’

“Chemists generally will welcome the decision of Council to award this medal to you because you have contributed a long and steady series of papers to our Transactions on subjects of the highest importance to the advancement of Chemical Science. Of these I would mention particularly your admirable investigations of the cyanine dyes and their uses as photographic sensitisers—information which proved to be of the greatest service to our fighting forces during the Great War—but more especially your researches on the occurrence of optically active forms of those substances which possess molecular dissymmetry such as the ketodilactone of benzophenone-2 : 4 : 2' : 4'-tetracarboxylic acid and the pyridylhydrazone of cyclohexylene dithiocarbonate.

“By these investigations you have definitely established the fact that the cause of the absence of optical activity among aromatic derivatives due to the uniplanar character of the benzenoid structure is no longer effective when two rings are joined in such a manner as to make them lie in different planes and you have recently emphasised this fundamental conclusion by resolving benzenesulphonyl-8-nitro-1-naphthylglycine and

thus showing that the inhibition of free rotation about a single bond leads to molecular dissymmetry.

"All this work has required the exercise of the highest attributes of the Research Chemist; infinite patience, high knowledge, clear reasoning, and great manipulative skill. It is, therefore, with the greatest pleasure that I hand you the Medal on behalf of the Council, and express the hope that you will continue in the future to add to your achievements by further enriching the science our Society was founded to foster."

Dr. MILLS made acknowledgment.

The Harrison Memorial Prize for 1929 was then presented to Dr. R. P. Linstead by the PRESIDENT, who said :—

"Dr. Linstead, it is my pleasant duty to present to you the Harrison Memorial Plaque and Prize which has been unanimously awarded to you by the Committee appointed under the Trust Deed, consisting of the Presidents of The Chemical Society, The Society of Chemical Industry, The Pharmaceutical Society, and The Institute of Chemistry.

"The description of the Award is best given in the words of the late Sir George Beilby, the Chairman of the Harrison Memorial Committee, who said 'with the balance of the sum collected (after defraying the cost of the War Memorial) it was decided to create a fund to provide, every three years, a prize of approximately £150, to be awarded to the Chemist, man or woman, not over thirty years of age, who shall have made the most meritorious original contributions to chemical science during the previous five years. It is to be given for distinguished research in any branch of chemistry, pure or applied, and no restriction is to be placed upon the manner in which the prize is to be utilised by the recipient.'

"It is seldom that a research worker within the age limits demanded by the Trust Deed strikes out a line for himself and does not merely elaborate and extend the research problems on which he has been trained. Nevertheless, during the period required by the Deed you have succeeded in devising and establishing on a sure basis a means by which it is now possible to determine the relative proportions of the constituents present in equilibrium mixtures formed by the interchange of the  $\alpha\beta$ - and  $\beta\gamma$ -structures of substances exhibiting three-carbon tautomerism, and have thus supplied a method by which the close and quantitative study of this fundamental phenomenon can be effected.

"In awarding this prize and plaque I have to remind you

## INCOME AND EXPENDITURE GENERAL PURPOSES

1928			Income.			1929		
£	s.	d.	£	s.	d.	£	s.	d.
60	0	0	To Life Composition Fees	...	...	...	...	172 10 0
			„ Annual Subscriptions:—					
912	0	0	Received in advance, on account of 1929	...	...	966	0	0
8313	0	0	„ during 1929	„	„	8061	0	0
565	17	0	„ „ „ „ 1928	...	...	474	0	0
39	0	0	„ „ „ „ 1927 and previous years	...	...	20	0	0
9827	17	0				9521	0	0
500	0	0	Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet	...	...	500	0	0
9327	17	0				9021	0	0
500	0	0	Add Arrears at date: £910; Estimated to realise as per Balance Sheet	...	...	500	0	0
	9827	17 0					9521	0 0
			„ Investments, Dividends on:—					
			£787 London, Midland and Scottish Railway 4 per cent. Debenture Stock	...	...	25	3	9
25	3	10	£1520 14s. 3d. Cardiff Corporation 3 per cent. Stock, 1914/54	...	...	36	10	0
36	10	0	£1400 India 2½ per cent. Stock	...	...	28	0	0
28	0	0	£2400 Bristol Corporation 2½ per cent. Debenture Stock	...	...	48	0	0
48	0	0	£2713 London, Midland and Scottish Railway 4 per cent. Preference Stock	...	...	86	16	4
86	16	4	£1200 Leeds Corporation 3 per cent. Stock	...	...	28	16	0
28	16	0	£1500 Transvaal 3 per cent. Guaranteed Stock, 1923/53	...	...	36	0	0
36	0	0	£1200 London and North Eastern Railway 3 per cent. Debenture Stock	...	...	28	16	0
28	16	0	£700 Canada 3½ per cent. Stock, 1930/50	...	...	19	12	0
19	12	0	£2100 5 per cent. War Stock, 1939/47	...	...	105	0	0
105	0	0	£1100 5 per cent. War Bonds, 1929/47	...	...	44	0	0
44	0	0	£800 Funding Loan, 4 per cent., 1960/90	...	...	19	4	0
19	4	0	£11212 9s. 3½ per cent. Conversion Stock	...	...	313	18	11
313	18	11						
829	2	2				819	17	0
—			„ Income Tax recovered	...	...	209	6	2
144	12	7	„ Income Tax recoverable	...	...	—		
60	11	6	„ Interest on Deposit	...	...	219	3	3
47	16	7	„ Miscellaneous Receipts	...	...	46	9	10
100	0	0	„ Editing Liversidge Papers (see contra)	...	...	—		
<u>£11,069 19 10</u>						<u>£10,988 6 3</u>		

## ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER 1929.

1928			Expenditure.	1929		
£	s.	d.		£	s.	d.
By Administration Expenses:—						
1456	7	11	Salaries of Staff ... ..	1550	6	3
290	12	6	Wages (Commissionaire, Housekeeper, and Charwomen)	289	13	6
51	2	8	Coal and Lighting ... ..	53	6	0
116	10	4	House Expenses and Repairs ... ..	75	16	9
19	13	6	Furniture ... ..	1	5	0
18	8	1	Telephone ... ..	22	6	5
15	2	5	Insurances ... ..	12	17	5
31	10	0	Accountants' Charges ... ..	31	10	0
8	0	0	Commission on Recovery of Income Tax ... ..	14	7	8
279	19	7	Miscellaneous Printing and Stationery ... ..	338	2	9
163	15	4	Postages ... ..	157	1	0
128	9	10	Superannuation of Staff ... ..	128	9	10
15	6	6	Congratulatory Addresses ... ..	11	9	0
80	12	11	Miscellaneous Expenses ... ..	41	9	9
50	0	0	Preparation of Inventory and Valuation for Insurance	—		
—			Legal ... ..	10	10	0
<hr/>				<hr/>		
2725	11	7		2738	11	4
121	14	1	„ Expenses of Meetings ... ..	162	4	6
99	11	2	„ Advance Proofs and Reports of Meetings ... ..	94	5	11
			„ Donations:—			
50	0	0	Federal Council ... ..	50	0	0
10	0	0	International Congress of Photography ... ..	—		
5	0	0	International Testing Association ... ..	5	0	0
<hr/>				<hr/>		
65	0	0		55	0	0
5807	16	10	„ Contribution to Publications Fund ... ..	5084	9	8
60	0	0	„ Transfer to ditto (Life Composition Fees) ... ..	172	10	0
1685	8	6	„ Contribution to Library Fund ... ..	1804	3	7
150	0	0	„ Transfer to Staff Pensions Fund ... ..	350	0	0
—			„ Transfer to Special Publication Fund (to form Sinking Fund for Collective Index, 1923-32) ... ..	500	0	0
100	0	0	„ Editing Liversidge Papers (see contra) ... ..	—		
254	17	8	„ Excess of Ordinary Income over Ordinary Expenditure carried to Balance Sheet ... ..	27	1	3

£11,069 19 10

£10,988 6 3

INCOME AND EXPENDITURE ACCOUNTS OF OTHER FUNDS FOR THE YEAR ENDED 31ST DECEMBER, 1929.

PUBLICATIONS FUND.														
Income.					Expenditure.									
1928					1929									
s.	d.	£.	s.	d.	£.	s.	d.	£.	s.	d.				
To Publication Sales:—					By Expenses on account of Journal:—					1929				
2761	13	2	Journals and Proceedings		1036	11	8	Editorial Salaries		...	1149	11	8	
2431	3	1	Abstracts		63	19	3	Editorial Postages		...	...	66	8	3
87	5	7	Collective Index, Vols. I-VI		544	7	7	Paper		...	...	463	0	11
838	18	6	Annual Reports on Progress of		8017	15	11	Printing of Journal		...	...	27	1	0
13	0		Chemistry		83	10	8	Bandings		...	...	90	0	12
6104	10	2	Other Publications		...	3	5	Addressograph Labels		...	...	386	13	10
547	19	5	Less Publishers' Commission		6096	16	7	Distribution of Journal		...	...	301	19	8
5566	10	9	Proceeds of Advertisements in		...	...	...	Insurance		...	...	5	13	5
72	18	8	Journals and Abstracts		678	0	0	Supernumeration of Staff		...	...	43	16	3
200	19	6	Less Commission		302	13	4	Miscellaneous		...	...	15	18	9
471	19	3	To Transfer from General Pur-		475	6	8	Expenses on account of Abstracts:—		...	...	5297	4	1
60	0	0	poses Account, being Life		...	...	...	Editorial Salaries (Bureau)		...	...	1100	16	9
85	15	6	Subscriptions		172	10	0	Editorial Postages (Bureau)		...	...	1336	17	8
100	0	0	Donation		183	3	3	Printing of Abstracts		...	...	2304	8	7
350	0	0	Government Publications Grant		100	0	0	Printing (Bureau £129 7s. 3d.)		...	...	363	11	11
			(through the Royal Society)		250	0	0	Index Paper (Bureau)		...	...	691	11	4
160	1	1	Dividend 80s. 11s. 6d. Con-		...	...	...	Bandings (Bureau)		...	...	124	7	9
			version 80s. 11s. 6d. Con-		171	19	7	for Index)		...	...	70	10	3
163	19	2	Ditto 2079 3s. 9d. War Stock,		163	19	2	Addressograph Labels		...	...	411	11	10
94	2	4	Ditto 2817 P. & O. Steam Naviga-		98	0	10	Distribution of Abstracts		...	...	57	6	10
10	18	1	tion Co. Deferred Shares		...	...	...	(Bureau £30 7s. 9d. for Index)		...	...	386	13	10
28	17	3	Ditto 186 51 Shares Lough (Syl-		3	17	11	Insurance		...	...	301	19	8
			vey) 3s. 0s.		...	...	...	Supernumeration of Staff		...	...	15	18	9
			Ditto 124 51 Shares Nedean Tea		5	9	0	Miscellaneous (Bureau		...	...	57	6	10
			Co.		6	6	10	£53 12s. 9d.)		...	...	6513	15	10
			Ditto 124 51 Shares Nedean Tea		6	6	10	Annual Reports on the Progress		...	...	615	15	0
			Ditto 124 51 Shares Nedean Tea		1	6	6	of Chemistry		...	...	4	15	0
			Ditto 124 51 Shares Nedean Tea		...	...	...	Purchase of Back Numbers of		...	...	143	14	9
			Ditto 124 51 Shares Nedean Tea		...	...	...	Publications		...	...	172	10	0
			Ditto 124 51 Shares Nedean Tea		...	...	...	List of Fellows—Printing, etc.		...	...	71	9	5
			Ditto 124 51 Shares Nedean Tea		...	...	...	Carried to balance sheet of		...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...	Life Composition Fund, viz.:—		...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...	Income Tax recovered (Net) Ped-		...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...	Income Tax recovered (Net) Ped-		...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...	Income Tax recoverable (Net) ...		...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...	Donations		...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 51 Shares Nedean Tea		...	...	...			...	...	—	—	—
			Ditto 124 5											









## THE CHEMICAL SOCIETY.—BALANCE SHEETS, 31ST DECEMBER, 1929.

GENERAL PURPOSES.				Assets.			
1928		1929		1928		1929	
£	s. d.	£	s. d.	£	s. d.	£	s. d.
<i>Liabilities.</i>							
To Subs. received in advance:—							
At £3							
968	0 0	968	0 0	859	3 7	859	3 7
" Sundry Creditors (Printing and other Expenses)				1650	0 0	1650	0 0
2,108	19 11	2,894	8 0	1316	1 0	1316	1 0
374	6 7	—	—	2070	2 0	2070	2 0
" Bankers' overdraft				3572	0 4	3572	0 4
" Excess of Assets over Liabilities as per last Balance Sheet				1143	1 0	1143	1 0
26,206	17 4	25,851	15 0	1400	13 6	1400	13 6
Add Excess of Income over Expenditure for Year				1033	11 0	1033	11 0
254	17 8	27	1 3	704	8 6	704	8 6
26,551	15 0	25,878	16 3	1995	0 0	1995	0 0
Deduct Transfers to Special Funds:—				1045	0 2	1045	0 2
Staff Pension Fund				480	0 0	480	0 0
Special Leases Fund				8487	2 2	8487	2 2
700	0 0	25,851	15 0	25,796	3 3	25,796	3 3
				3,003	5 7	315	1 6
				600	0 0	500	0 0
				2	12 8	6	8 8
				229,301	1 6	1,043	13 6
				229,002	6 10	2,000	0 0
				229,301	1 6	229,662	6 10

By Investments (value when acquired):—  
 £787 London, Midland and Scottish Railway 4% Debenture Stock ...  
 £1920 India 2½ per cent. Stock ...  
 £2400 Bristol Dock Account ...  
 £2713 London, Midland and Scottish Railway 4 per cent. Preference Stock ...  
 £1300 Leeds Corporation 3% Stock ...  
 £1500 Transvaal 3 per cent. Guaranteed Stock, 1923-25 ...  
 £1200 London and North Eastern Railway 3 per cent. Debenture Stock ...  
 £700 Canada 3½% Stock, 1930/50 ...  
 £2100 5 per cent. War Stock, 1929/47 ...  
 £1100 5% National War Bonds, 1929/47 ...  
 £600 4 per cent. Funding Loan, 1960/60 ...  
 £11,312 8s. 5½ per cent. Conversion Stock ...  
 (Market Value £20,849 3s. 8d.)

Sundry Debtors ...  
 Subscriptions in Arrear, £910. Estimated to realise ...  
 Cash in Hand ...  
 Cash at Bankers, Current Account ...  
 Cash at ditto Deposit Office ...

**RESEARCH FUND.**

1928.		1929.		1928.		1929.	
£	s. d.	£	s. d.	£	s. d.	£	s. d.
<b>Liabilities.</b>				<b>Assets.</b>			
To Sundry Creditors ...				By Investments (value when acquired):—			
" Excess of Assets over Liabilities as per last Balance Sheet ...				£1000 London and North Eastern Railway 4 per cent. 2nd Guaranteed			
14,486	13 4	14,564	19 9	1010	0 0	1010	0 0
Add Excess of Income over Expenditure for Year ...				1049	15 11	1049	15 11
98	7 5	—	—	£1034 Gt. W. & T. Ry. 2½% Debentures			
Less Excess of Expenditure over Income for Year ...				1000	0 0	1000	0 0
—	14,564	35	4 5	£1143 16s. New South Wales 5 per cent. Stock, 1935			
				1002	16 9	1002	16 9
				" Metropolitan Water Board 3 per cent. " B " Stock			
				1508	8 6	1508	8 6
				706	6 2	706	6 2
				4267	4 10	4267	4 10
				3398	14 10	3398	14 10
				14,443	2 0	14,443	2 0
				49	13 8	49	13 8
				74	13 8	74	13 8
				£14,567	9 5	£14,567	9 5
				Sundry Debtors ...			
				Cash at Bank, Current Account			
				— 86 13 4			
				£14,529 15 4			

THE EDWARD FRANK HARRISON MEMORIAL TRUST FUND.

To Excess of Assets over Liabilities as per last Balance Sheet		By Investments (value when required) —	
11118 4 4	...	500 0 0	£500 National War Bonds 5% 1929 ...
50 11 8	...	500 0 0	£527 10s. Treasury Bonds 6% 1933/6 ...
—	...	50 1 5	£1 15s. 8d. 31% Conversion Stock ...
	...		£1265 London Midland & Scottish Railway 4% Debenture Stock ...
	...		(Market Value £,1005 19s. 1d.)
11183 16 0	55 19 11	1050 1 5	1051 6 6
	1267 18 1	18 14 7	
		100 0 0	
			Cash at Bank ...
			Do. ...
			Current Account ...
			Deposit Account ...
			26 10 2
			140 0 0
£1168 16 0		£1168 16 0	
£1267 18 1		£1267 18 1	
1101 7 11			
166 10 2			
£1267 18 1			

**STAFF PENSIONS FUND.**

	To Sundry Creditors	By Investments (value when acquired):—			
401 12 9	...	£289 4s. 4d. 3½% Conversion Stock ...	226 12 9	...	226 12 9
	...	as per last Balance Sheet ...	375 0 0	...	375 0 0
59 4 10	...	Add Balance of Income over		...	...
	...	Expenditure for Year ...	39 4 10	...	38 1 3
200 0 0	...	Add Transfer from General	—	...	390 0 0
	...	Purposes Account from ac-		...	...
	...	cumulation of Funds ...	907 14 0	...	428 1 3
640 17 7	...		—	...	...
£640 17 7	...		£1029 14 0	...	£1029 14 0



that they were founded to commemorate an exceptional man who gave his life for his country just as surely as if he had been killed on the field of battle and to express the hope that throughout your life you may be guided by his high sense of service and his great devotion to duty."

Brief acknowledgment was made by Dr. LINSTEAD.

The PRESIDENT delivered his Address, entitled: "Internal Co-operation." A vote of thanks to the President for his services in the Chair during the past year and for his Address was proposed by Professor H. B. BAKER and seconded by Professor W. P. WYNNE. This was carried with acclamation and acknowledged by the PRESIDENT.

It was announced that the following had been elected to fill the vacancies on the Council for the year 1930—31 :—

*President.*—J. F. Thorpe.

*Vice-Presidents who have filled the office of President.*—P. F. Frankland, A. Scott.

*Vice-Presidents who have not filled the office of President.*—A. Lapworth, F. L. Pyman.

*Ordinary Members of Council :—*

*Town Members :* T. J. Drakeley, R. H. A. Plimmer, C. K. Tinkler.

*Country Members :* H. M. Dawson, E. Hope, J. Kendall.

## PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, March 27th, 1930.

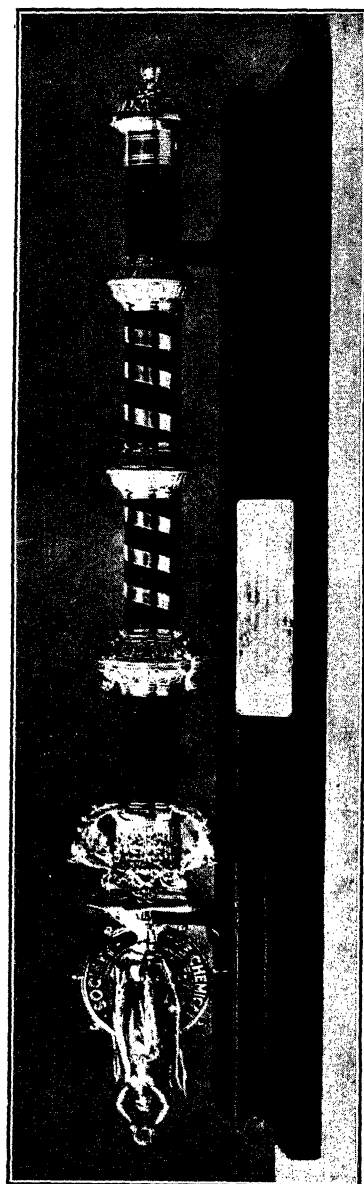
By JOCELYN FIELD THORPE, C.B.E., D.Sc., F.R.S.

### *Internal Co-operation.*

I FIND, on looking through a number of Presidential addresses given before the Society in the past, that usually it has been the custom to devote the address given at the end of the second and final year of office to matters relating to the progress of the Society during the previous two years, leaving the earlier or first address to deal either with some subject of scientific interest with which the President was personally familiar or with the discussion of some wide problem which, at the moment, was of general interest to the Fellows. The Fellows have elected me to another term of office, and I am grateful to them for doing so, because it shows that they have a certain confidence in my desire to further the interests of the Society during the difficult period that is before us. Nevertheless, I am fully determined to take advantage of the permission accorded me to submit my resignation to the Council at the end of the first year of the new period, so that the present occasion constitutes not only the second address of the first term but also the first address of the new term, and next year I shall be in a position to survey the progress made by the Society during my three completed years of office. It is my intention, therefore, to use this occasion to express views and opinions on certain aspects of our Science and to elaborate certain matters which formed the subject of my address at Leeds last year.

### *The Need for Uniformity of Effort.*

In my address to the Society last March I dealt with Co-operation in Science and Industry. It is my intention to-day to deal with the more intimate matter of internal co-operation, affecting as it does the immediate future of the Society. In the previous address it was stated that "the war, although one of the greatest economic disasters the world has yet experienced, gave, without question, a stimulus to discovery and production which no other event could have occasioned." The war did more than this, for it showed the results and achievements which could be accomplished by united efforts towards a common end. The world needed such a lesson, and the amazing development in Science and Industry that has taken place since that great upheaval must be ascribed to the fact that the nations are now applying the lessons learnt in war to the more settled but not less arduous conditions of peace. Indeed, the spirit



Reproduction of Mace presented by Mr. Ayerst Henham Hooker, F.I.C., on January 16th, 1930.





of co-operation or rationalisation is now directing human progress in numerous directions, and not only is leading to internal co-operation within specific branches of activity, but is causing many groups dealing with related subjects to join together in their own and in the national interests. For it is certain that the next twenty years will witness a struggle for supremacy in scientific effort and in the industrial application of science throughout the world which will be even more intense than was the struggle between the contending nations during the war, and that only those nations will succeed in this struggle who have equipped themselves with knowledge and with the ability and foresight to apply that knowledge by united effort towards the achievement of a common purpose.

### *The Need for a Scheme.*

In the previous address it was pointed out that it is chiefly to the chemical and allied industries—mining and metallurgy—that the country turns for the utilisation of its potential productive capacity, because it is their function, aided by the engineer, to make available its mineral, vegetable, animal, and atmospheric wealth. It must be recognised, therefore, that the separation into isolated units of the organisations dealing with the scientific and technical development of the three basic industries mentioned—namely those of Mining, Metallurgy, and Chemistry—is not in accordance with the existing state of scientific knowledge, and that the Nation and Empire cannot utilise to the full the forces inherent in them unless some scheme can be devised by which close co-operation between these groups can be effected. Such a scheme would have to be framed so as to enable the constituent organisations to retain their autonomy, but it should be drawn up in such a manner as to ensure that full opportunity would be afforded for general intercourse and discussion.

At the present time the organisations dealing with the subjects mentioned above are housed—some very inadequately—in various parts of the metropolis, and there are few facilities for the interchange of thought and ideas. There is no general meeting-room, and although most of the Societies and Institutions involved have libraries sufficient for the immediate daily needs of such of their members as are resident in London, such libraries are scattered and are not readily available for anyone who wishes to obtain information, even on specific subjects, and especially on those related to border-line enquiries. Data connected with matters not immediately within the province of any one particular subject but belonging to two or more of them are at present difficult to find. A general Library and Information Bureau is therefore one of the chief requirements of the Scheme: others are a Central Meeting-Room,

secretarial offices closely in touch with one another, and such provision for social amenities as may be necessary to permit of intercourse between the members of the various branches during their leisure moments and to provide a centre for visitors from overseas.

In the chemical world the need for such a scheme has been recognised for ten years past, and efforts have been made from time to time to give effect to it. But, for one reason or another, each scheme has failed to reach fruition, mainly because it involved the raising of capital by means of a loan or some other form of financial commitment which it was felt unwise to ask the various Societies and Institutions to bear.

The Societies dealing with Chemistry, as indeed those dealing with other branches of science and industry, are not wealthy bodies. Most of them possess a small accumulated capital, but the main source of income is the subscriptions derived from their members. The chief item of expenditure is the cost of their publications, the administrative expenses being comparatively small. It is only by the exercise of rigorous economy that it is possible to provide for a small credit balance at the end of each year, and it would therefore be unwise to saddle the Societies with a debt which would necessitate the payment of interest and the creation of a sinking fund. Any scheme therefore which could be regarded favourably as a means of linking up the Chemical Societies under one roof would involve the collection of a sufficient fund by public subscription, and, hitherto, the sum regarded as necessary for this purpose has been too large to be within the sphere of practical accomplishment. The need, however, is urgent, because other nations, notably the French, are actively engaged in co-ordinating their chemical activities, and the Americans already have their "Chemists' Club" in New York. Unless, therefore, something is done, and that quickly, we shall be handicapped in the struggle with which we are faced.

Former Presidents have emphasised the need for such a scheme on the part of our own Society, and even twenty years ago it was regarded as inevitable. The reason for this is that our apartments in Burlington House, which were given us rent free by the Government fifty years ago, have long since ceased to provide us with adequate accommodation. The meeting-room is too small, and is incapable of being suitably ventilated. The seating, which has been arranged so as to give the maximum seating capacity, is unsuitable. Everyone who has occupied this Chair and who has witnessed the contortions necessary to enable the occupants of the cross benches on the west side to see the screen will have sympathised with those who have had to seat themselves there. On occasions,

such as those of our special lectures, we cannot use this meeting-room owing to lack of space, and have to seek accommodation elsewhere. The Library is now so overcrowded that recourse has to be had to shelving books in double rows—a most undesirable procedure. Moreover, all available space throughout the building—including the cellars—has to be used for the storage of books, involving in the case of cellar storage possible loss by flooding, which cannot adequately be covered by insurance. The other Chemical Societies have no accommodation other than office facilities and for the most part make use of our meeting-room. There must, therefore, be general agreement, apart from reasons of national policy, that the need for new quarters is imperative. Indeed, the change in the case of the Library cannot be longer delayed, as the normal increase represents some 900 volumes yearly.

A scheme is now about to be launched by which, for a sum approximately half that required for new premises under the older projects, the Society may be housed in a "Chemistry House," together with the allied organisations, the Society of Chemical Industry, the Institution of Chemical Engineers, and the Institution of the Rubber Industry. This scheme is of such vital interest to every member of these Societies that I make no apology for outlining it to you and discussing its most important practical aspects.

#### *The Proposed Scheme.*

Two years ago a scheme was started having for its object the housing together of the chief Societies and Institutions connected with the scientific and technical development of the mining and metallurgical industries, namely :—

- The Empire Council of Mining and Metallurgical Institutions ;
- The Institution of Mining and Metallurgy ;
- The Institution of Mining Engineers ;
- The Iron and Steel Institute ;
- The Institution of Petroleum Technologists ;
- The Institute of Metals ; and
- The Institute of Fuel,

the idea being to house these bodies under one roof in much the same manner as had already been accomplished by the Civil and by the Mechanical Engineers. In June of last year it was considered that the scheme could not be complete and effective without the inclusion of the Chemists, and the Councils of the Chemical Society, the Society of Chemical Industry, the Institution of Chemical Engineers, and of the Institution of the Rubber Industry were approached to collaborate. Each Council agreed to join the scheme on the understanding—

- (1) That the money asked for by public subscription was forthcoming;
- (2) That adequate accommodation was provided.

It was agreed to appoint three members from each Council to serve as a Committee, the function of which was to prepare plans and formulate a scheme for the provision of a "Chemistry House."

The original plan as contemplated by the Societies representing Mining and Metallurgy provided for the occupation of three-fifths of a site situated in Victoria Street, Westminster. The site is the property of the Ecclesiastical Commissioners, who are prepared in principle to grant a long lease at a ground rent which it is within the capacity of the constituent Societies to pay. As soon as the Chemical group signified their intention of participating in the scheme it was agreed that the whole site should be taken up, the two-fifths remaining over from the original scheme being assigned for the purposes of the Chemical group, and becoming therefore the "Chemistry House" of our requirements. The approximate cost of acquiring the existing lease of the site, which has twenty-two years to run, and of erecting a suitable building thereon has been estimated, after careful enquiry, at £325,000. This sum, however, does not provide for furnishing the new building, so it has been agreed to issue an appeal for £350,000. In other words, two-fifths of this sum, or £140,000, will have to be provided by the Chemical group as its share towards the complete cost. It has been arranged that the ground rent shall be paid by each Society contributing yearly an amount equal to but not more than it pays as rent for its present premises, and as this amount will certainly be more than that required to pay the rent, the excess will be utilised to defray the cost of upkeep and the expenses of services common to all Societies housed within the building.

#### *Area Available.*

The total "carpet" area available in the new building will be approximately 8,500 square feet for each floor. One complete floor will be occupied by the general Library and the whole of the top floor will be utilised as a restaurant and club. There will be a large Meeting Hall to hold 500 people in the main portion of the building, probably on the ground floor opposite the main entrance. This will leave five floors available for the Societies entering into the scheme, and in the case of "Chemistry House" these floors will have two-fifths of 8,500 square feet, or 3,400 square feet each. There will be a smaller meeting-room—to hold 200—in the Chemistry wing for the use of the Chemical group, although the group will have the use of the larger meeting-room when occasion requires. It is evident,

therefore, that the space available is more than adequate for the needs of the Societies entering into the scheme and provides ample room for expansion. In order, however, that the building should be occupied from the start, it has been arranged to let such space as may be available to "Tenant" Societies who would hold leases for an agreed period and pay an agreed rent. Thus, in the Chemical wing, the Chemical Society and the Society of Chemical Industry would each occupy one floor of 3,400 square feet. The Institution of Chemical Engineers requires only 1,200 square feet, so on the floor occupied by this Institution there would be 2,200 square feet available for the Entrance Hall, Ante-Room, and Meeting-Room. The Institution of the Rubber Industry has intimated that it requires only 1,000 square feet of space, so the remainder of the space on its floor, together with one complete floor, or 5,800 square feet in all, will be available for "Tenant" Societies of the Chemical group. These "Tenant" Societies will be in every case entities directly connected with the industries represented by the constituent bodies. They may include the Association of British Chemical Manufacturers, the National Federation of Iron and Steel Manufacturers, and the Mining Association of Great Britain, and other groups of the same category.

#### *The Library.*

As already mentioned, one complete floor throughout the whole building will contain the General Library. This Library will include the Libraries already in the possession of the constituent Societies, and the 33,000 volumes now in our possession will be handed over to form the nucleus of the new Library. In consideration of this it has been agreed that our Society shall continue, as in our present quarters, to be housed rent free. The Library will be sectionalised, and each section will remain under the control of the sectional Librarian. In effect, therefore, our Library, Librarian, Library staff, and Library Committee will continue to function in the new building in the same way as they do now. Moreover, there is no reason to anticipate that there would be any falling off in the outside contributions to the upkeep of our Library. The constituent Societies would continue as a matter of course to pay their share, and outside bodies would be even more anxious to contribute than they now are, owing to the increased facilities provided.

The Central Library is, indeed, one of the chief features of the scheme. It will contain at the beginning some 70,000 volumes exclusive of pamphlets, and will probably be augmented by some 2,000 volumes yearly. The inevitable overlapping between scientific and technical Libraries in respect of books and periodicals dealing with borderland subjects will disappear, or, alternatively, will

provide duplicate copies which can be utilised for the purpose of lending. There will be an efficient Bureau of Information by whose aid the enquirer will be directed to the source from which the information he requires can be obtained. In fact such a Library will be unique in its completeness and accessibility and will be a point of attraction not only for business men and students at home, but also for those visitors from overseas who desire to keep themselves abreast of modern developments in the subjects dealt with. No one can foresee what effect such a source of information, and indeed of power, housed centrally and easily accessible, may have on the future development of Science and Industry.

The restaurant on the top floor will be the means by which meetings under social conditions can be arranged. It is intended that there shall be several small dining-rooms in which the existing dining clubs of the various Societies can meet, leaving the larger restaurant and dining-room for general purposes. The Chemical Industry Club and the Oil Industry Club have now under consideration the question of joining as "Tenants." Should they decide to do so, special rooms would be provided for them on the top floor. The Clubs would, however, retain complete autonomy and would be "private" in the sense that only those persons whom they decided to elect as members could use their premises.

#### *General.*

It seems, therefore, that at last we are in a fair way to realise the "Chemistry House" of our needs at a cost which is about half that which would be necessary if Chemists were forced to act alone. This achievement has been possible only because the present spirit of collaboration and the desire towards uniformity of effort have caused the various Societies and Institutions which are parties to the scheme to come together to form a solid band. Ten years ago it would probably have been impossible to do this, and if the present effort fails it may be another fifty years before conditions are again favourable.

The economic advantages of the scheme will be numerous. Many details of office organisation can be pooled, service can be shared along general lines. Internal printing, such as the printing of notices, circulars, and so forth—an expensive item under present conditions—can be done in a small printing press on the premises, and other economies can be effected in several directions. Let us therefore exert all our energies to take advantage of the moment, and do everything in our power to further a project which cannot but be fraught with good for all of us and for the Nation and Empire as a whole; each of us doing what he can to further the cause by

contributing what he is able to contribute, but more especially by convincing those who are in a position to help substantially that the scheme is vital to the future of organised Science and Industry in this country.

*Financial.*

The problem of raising the necessary money causes some anxiety in view of the present great depression of industry and the incidence of high taxation. In any case, the general appeal cannot be launched until after the Budget. We must look to the industries concerned to provide the greater proportion of what we require, and we hope that they will regard it as being to their advantage to do so, and will also look on it as a kind of thank-offering for past services and for the manner in which the Scientific and Industrial Institutions have provided them with information in the past. It is not too much to say that no Chemical Industry would exist to-day if there had not been the free interchange of thought and information which the Societies have been formed to promote and foster. Not that I have found any marked desire on the part of those engaged in industry to repudiate this debt; on the contrary, except in one or two instances, I have found, as Chairman of the Appeal Committee, not only a desire, but even eagerness to do all that was possible. It is rather the air of uncertainty that pervades all things industrial at the moment that prevents many definite promises being given. Nevertheless, when the general appeal is issued it will contain a list of definite promises amounting to £130,000, including some munificent personal donations, such as £10,000 from Mr. Robert Mond, £1,000 from Mr. Emile Mond, £1,000 from Sir Robert Hadfield, £250 from Sir Charles Parsons, and £105 from Mr. Horatio Ballantyne. A petition was sent to the Chancellor of the Exchequer asking for a Treasury contribution. Such a petition involved no new principle, since, by the housing of a number of Societies in Burlington House, the Government of that day admitted its obligation to Science. Seeing that one of the petitioning Societies, our own, would vacate the premises then allotted to them, it seemed a simple extension of the principle involved to ask for some monetary consideration. A deputation waited on the Financial Secretary, being introduced by the President of the Royal Society, and several speakers laid the case before him. The answer, however, was "non-possumus," although sympathy was expressed with the object in view. It is possible that another appeal made in more favourable circumstances may meet with a different answer, but it seems that we must rely for some time to come on ourselves, and on those of our friends who sympathise with our desire to give effect to the scheme.

*Domestic Co-operation.*

In my previous address I discussed at some length the advantages which were likely to accrue through the formation of larger combines in industry. I did not do much more than mention at the time the benefits which might be expected to attend a similar process in Chemical Science, because I felt that the time was not then suitable to discuss so difficult a problem. Nevertheless, I did call attention to the advantages enjoyed by the American nation in having but one Chemical Society which could speak for the whole of Chemistry and regulate its publications and conferences. Since then the situation has changed considerably owing to the elaboration of the scheme described above for housing the Chemical Societies under one roof, and I feel that I shall not be guilty of an indiscretion if I examine for a moment the manner in which it might be possible to give effect to that outward and visible sign of union which is now contemplated. It is not my intention to suggest that any such system as that found in the United States is now applicable in this country, because there is no doubt that the principle of combined effort, although admirable and effective in certain directions, contains features which are not altogether desirable. Partial de-centralisation is often more effective than complete centralisation. For example, it would be undesirable and, indeed, impracticable to have the same President, Officers, and Council of the Chemical Society and the Society of Chemical Industry. It would be a practical impossibility to find the men who could give the time adequately to fill these offices. I am speaking on my own behalf, and I am sure also on behalf of my friend the President of the Society of Chemical Industry, when I say that most of our leisure moments are occupied by the business of the Society we serve and that we should not contemplate with equanimity any suggestion that either of us should take over the work of the other in addition to his own. Any such step would tend to throw the control of the combined Societies into the hands of salaried officials, and many of us feel that so long as we can get competent men able and willing to give the time to act in honorary capacities it is desirable to do so.

When the Society of Chemical Industry was formed as a separate entity in 1881, it took over certain definite functions which it has since performed in accordance with the terms of its constitution. The terms Scientific and Technical possessed in those days very definite meanings, and they still possess, or have had attached to them by custom, meanings which enable a decision to be reached, on broad lines, as to the matters falling within either sphere. It is possible to say, in clear cases, whether any communication is scientific in the sense that it deals with the elaboration of some



subject on lines which, for the moment, may be regarded as based on purely scientific hypothesis or theory or whether it is technical in that it is concerned with the description of some chemical operation of acknowledged mechanism carried out on the large scale. It is rather in the matter of the discussion of such questions that co-operation can, in the first instance, be effected. Formerly there was a fairly distinct line of demarcation between the Scientific Chemist and the Technical Chemist, but to-day it is doubtful whether any Scientific Chemist exists who is not interested on the technical side, and the Technical Chemist who is not interested on the scientific side is becoming increasingly rare. Indeed, the whole trend of modern development is to diminish the difference between these two types, and in the not distant future this difference will entirely disappear.

### *The First Step to Reunion.*

The first step towards co-operation between the two branches of our science must be one that will lead to conditions which will enable papers to be read and discussion to be held on both technical and scientific subjects by all those who have the interests of both sections at heart. Such joint meetings must be so arranged that persons interested in both aspects may be present and speak. Here in London such facilities already exist, but they are not yet sufficiently wide in character. I would suggest, therefore, as a first step, that meetings of the four constituent bodies forming the Chemical wing of the new building, namely the Chemical Society, the Society of Chemical Industry, the Institution of Chemical Engineers, and the Institution of the Rubber Industry, should be open to all members of those Societies and Institutions. Such a proposal applies also to those "Tenant" Societies who intend to use the Chemistry wing.

In the provinces, where there are not so many meetings, it would be necessary to arrange composite programmes, so that not only would members of all the constituent Societies be able to attend and take part in the discussions, but also the local Committees controlling such meetings should themselves be composite bodies. The Chairman or President could be chosen from one or other section as circumstances permitted, as could also the Secretaries, although for the immediate future a system of joint Secretaries might, with advantage, be inaugurated.

In effect, therefore, the suggestion is that membership of any one "constituent" or "Tenant" Society under the new scheme should confer on the member the right to read papers and to attend meetings of each Society, whether held in London or as sectional

meetings in the provinces, and that the programmes provided at the sectional meetings should embrace subjects on both the scientific and the technical side. This suggestion must be taken in conjunction with further suggestions which will be made later and in which a scheme is outlined for determining the conditions of membership of the Societies.

### *Publications.*

It may be assumed that one of the chief reasons why a person belongs to one or more of the Chemical Societies is to obtain their publications. If this is so, it may well be that the cause of the annual drop in membership which some Societies are now experiencing may be due to the increased facilities afforded by works' libraries in supplying the requirements of their staffs. Indeed it has been said that some firms have notified their employees that the need for joining Societies no longer exists, because their own libraries contain all the required literature. The large General Library, which is the chief feature of the new housing scheme, should undoubtedly serve as an attraction and inducement for new members to join at least one of the constituent Societies, but unless there exists in the future as there has existed in the past a general desire among the younger men to join the Societies as a matter of principle, it is to be anticipated that a general decline in membership will occur.

The publications of the two chief Chemical Societies are :

- (1) The Journal of the Chemical Society, containing the Transactions of the Society;
- (2) The Proceedings of the Chemical Society, containing mainly matters concerning the business of the Society;
- (3) The Journal of the Society of Chemical Industry;
- (4) Chemical Abstracts A (pure) and B (applied);
- (5) "Chemistry and Industry."

"Chemistry and Industry" contains under one cover the Transactions of the Society of Chemical Industry and the B Abstracts. There are other incidental publications such as the Annual Reports, but as the cost of these is, at present, defrayed by sales, they need not be considered for the moment.

The publications of the American Chemical Society are similar in character, being the Journal, Chemical Abstracts, Industrial and Engineering Chemistry, and its News Edition. There is no official British equivalent to "Industrial and Engineering Chemistry," but there is a periodical very similar to it in general appearance called "The Industrial Chemist," which is published by a London firm. In my opinion steps should be taken to ascertain whether it might

not be practicable to rearrange the publications of the two Societies in the following way :

- (1) Chemical Transactions. To contain the Transactions of the Chemical Society and the Transactions of the Society of Chemical Industry in those cases where no elaborate illustration of plant or apparatus is required (published monthly).
- (2) Abstracts A and B published together.
- (3) A publication on the lines of "Industrial and Engineering Chemistry" to contain the Transactions of the Chemical Society and of the Society of Chemical Industry in those cases where elaborate illustration of plant or apparatus is required (published monthly).
- (4) "Chemistry and Industry"—the news edition—(published weekly containing the Proceedings of the Societies).

Publications 2, 3, and 4 should yield considerable revenues from advertisements—especially (3), and it is possible also that this publication might be regarded by the Institution of Chemical Engineers as a means of issuing its more elaborate papers.

It is not my intention to suggest ways and means by which the above result can best be accomplished. Such a problem will have to be most carefully investigated by a Joint Committee of both Societies, but it cannot be denied that there is a certain degree of unnecessary duplication between chemical publications as a whole, and that if this duplication could be removed and the various publications consolidated an increased circulation would be attained, especially among the outside public, with a consequent increase in the number and quality of the advertisements. The object to be achieved is the unification of our chemical publications by bringing together under an Editorial Board the publications of two and possibly more constituent Societies, and to include with these such outside publications as circumstances may permit.

#### *Finance.*

It is assumed that the publications mentioned above could be carried into effect for the same or a less sum than that now necessary to produce the existing publications of the two Societies. Now, the total membership of the Chemical Society and the Society of Chemical Industry, allowing for those members who belong to both, is of the order of 8,000,\* and the main question that arises is this, Is it possible that a reduction in the present rates of subscription to the two Societies could economically be effected in the case of joint membership of both Societies? For example, would it be financially possible to allow all joint members the right to receive

\* In this and similar cases I have purposely kept to round numbers.

the publications suggested above on payment, say, of a subscription of £3 10s. instead of the £5 10s. which they would pay under present conditions? \* The obvious answer to this question is that any such scheme would have to be retrospective and include those members who already belong to both Societies—some 1,000 in all—leading to a considerable loss of revenue. This, however, need not act as a deterrent to the introduction of the new system, because the 3,000 members of the Chemical Society who are not now members of the Society of Chemical Industry and the 4,000 members of the Society of Chemical Industry who are not now members of the Chemical Society would have the option of paying the composite fee and receiving the full benefits provided, but those who do not take advantage of this option would have to give extra payment for such publications as they may require over and above those to which their individual subscriptions entitle them.

The chief hardship would undoubtedly rest with those who are already members of both Societies, because, as stated previously, the Societies could not face the financial loss entailed by those members paying a composite fee which would be considerably less than they now pay to both Societies. A change such as that contemplated must be gradual, and no action must be taken that will lead to a sudden drop in the annual income of either Society.

For the time being, therefore, the members who already belong to both Societies would have to continue to bear the cost of the full subscription to each Society, and the reduced or joint contribution could only be made operative in the case of new members.

The essence of the proposed scheme is that *new members must be required to join both Societies*. It is true that the present joint members might easily resign and re-join under the new scheme, but this would have to be prevented by Regulation. The joint contribution of £3 10s. which I have suggested is purely tentative: the right figure can only be determined by the Joint Committee of the two Societies with actuarial help. I have merely suggested it to form the basis of investigation, but I do not think it is far wrong.

For many years to come there would, therefore, be the following classes of members :

- (1) New members who must join both Societies at a composite fee of, say, £3 10s. annually.
- (2) Old members of the two Societies who would continue to pay (ex gratia) their present contributions to both Societies.
- (3) Old members of each Society who would continue to pay their present contributions as members of each Society and remain such unless they signified their desire to become

\* It is suggested that all entrance fees should be abolished.

joint members, when they would pay the composite contribution of £3 10s.

Those who decided still to remain members of each Society would continue to pay the subscription required by each Society, but such members would receive, free of charge, only those publications which each Society regarded as adequate.

If, therefore, this scheme is workable actuarially and is agreed to by the Societies concerned, it means that after the lapse of, say, thirty years, membership would be confined to Class 1 only, and the two Societies, while having their own President, Officers, and Council, and thus retaining complete autonomy as regards organisation and finance, would have a common membership and joint publications. The scheme must be examined carefully by an actuary, but it is thought that the loss of revenue, due to the composite subscription, would be more than compensated for by the increase of membership due both to new members joining and to those old members of Class 3 who elect to become joint-members. Personally, I feel some sympathy with the members of Class 2, being one of them myself, but I feel sure that most of them will realise that the action suggested is necessary in the interests of co-operation.

Let us therefore devote our energies in the immediate future firstly towards making the scheme for a central House an accomplished fact not only by giving help ourselves, but also by inducing others to help. It must be remembered that the membership of the constituent bodies combined in the scheme amounts to over 20,000, and that if each of these members acts in the manner suggested above a substantial sum towards the cost of the scheme will be forthcoming. Secondly, let each member of our two Societies do what he can to further the scheme of amalgamation, based on some such plan as I have outlined in this address. Difficulties there are sure to be, but most difficulties of detail can be settled when the broad outlines of the scheme are established.

There is undoubtedly a strong feeling among members of both Societies that the time has now come to close, in some measure, the break made in 1881. If that feeling is real and if strong opposition is lacking from either side we shall achieve the object in view and bring about a union which circumstances now favour and which, in the opinion of many of us, is in accordance with the best interests of the two Societies and of Chemistry generally. If no union can be effected at the present juncture it will be due to opposition from within, and those opposing must remember that the same set of conditions is not likely to recur for many years to come and that failure under the very favourable circumstances of the moment will probably mean complete failure hereafter.

We have, in effect, the opportunities of forming a Chemical Society divided into two administrative sections, each section autonomous as regards internal administration and finance but with unified publications and a membership gradually becoming common to both. The Councils of the two sections would continue, as hitherto, to deal with routine administration, leaving the work of the section to be carried out, as at present, by Committees of Council. Financial matters would have to be arranged "pro rata" by a Joint Financial Board, but each section would have its own Finance Committee for the purpose of financial administration within its own domain.

The Publication Committees of each section would continue to function as now and would determine which of the communications submitted to them should be published and in which publication. There would have to be a joint Editorial Board composed of members of both Councils, whose duty it would be to direct the publications issued jointly.

The Bureau of Chemical Abstracts, which under the proposed scheme will deal with the unified abstracts and the joint indexes, would continue to act as it does at present and would retain its present constitution. The Library Committee would also retain its present form and carry out its work in the same manner.

Regarding the two other constituent Societies, the Institution of Chemical Engineers and the Institution of the Rubber Industry, the former has already expressed its wish to be associated with British Chemical Abstracts, and it may be possible that the variety and scope of the other publications for which provision is made under the scheme will appeal to this body as a suitable means for publishing its scientific and technical communications. If this should happily be the case, the Institution would have to be represented on the joint Editorial Board and on the joint Finance Board. Unfortunately, it is not possible in this case to arrive at a common membership, since the Institution is, in part, a professional body, the membership of which carries a qualification. So far as the Institution of the Rubber Industry is concerned steps must be taken to ascertain in how far and in what manner it is prepared to be associated with the scheme.

It will probably require twelve months' work on the part of a joint Committee to elaborate all necessary details and explore every avenue leading in the desired direction, but let us be ready, when the fiftieth anniversary of the foundation of the Society of Chemical Industry occurs next year, to put forward a well-conceived and agreed plan of amalgamation which can be put into operation at once.

*The Dyestuffs Act.*

In my address last year I mentioned the Dyestuffs (Import Regulation) Act as illustrating one of the ways in which Government could co-operate in order to protect "young and struggling industries against competition from similar but established industries abroad." This Act was passed in December 1920 and came into force on January 15th, 1921. It prohibited, for a period of ten years, the importation into the United Kingdom of all synthetic dyestuffs and all intermediate products used in their manufacture, but permitted certain materials not available in this country to be introduced by licence.

The Act, which has been of very great value in assisting the establishment of a Dyestuffs industry in this country, comes to an end, therefore, at the close of this year, unless it should be extended for a further period.

There is perhaps a tendency in certain quarters to-day to consider the Dyestuffs industry only from the point of view of the supply of dyestuffs to the colour users. There is, however, another very important aspect to which we as members of the Chemical Profession must give full consideration. I refer to the fact that a successful and well-established Dyestuffs industry establishes in the country having such an industry a certainty of development in the field of organic chemistry. Firms are enabled to create large research organisations employing many of the most capable chemists in the country, and from these organisations there arise all kinds of organic developments, not alone in dyestuffs, but in very many other branches of industry.

Such Research Organisations are recruited from the Research Schools in our Universities and University Institutions, leading not only to the employment of many research chemists trained therein, but also to their own development.

The history of the great German dye firms in the past has shown this clearly, since most of the successful lines into which these firms have ventured have arisen from research work carried on originally for the Dyestuffs industry. It appears important, therefore, that a broad view should be taken of the establishment of a Dyestuffs industry, and that full weight should be given to the importance to the nation of the development of Organic Chemistry.

During the Great War the importance of this was clearly seen, for not only did the great German Dyestuffs firms assist from the military point of view—they also operated very extensively in regard to many organic developments which were of an entirely civil character.

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## OBITUARY NOTICES.

## FREDERICK WILLIAM DOOTSON.

BORN AUGUST 10TH, 1863; DIED DECEMBER 12TH, 1929.

By the untimely death of F. W. Dootson at the comparatively early age of 66 years, the University of Cambridge lost an able and devoted teacher and his friends in the Chemical Laboratory a congenial and gifted colleague.

There is little of general interest to record about Dootson's earlier years, but his connexion with Cambridge dates from 1891, when he entered Fitzwilliam Hall as an undergraduate. Shortly after graduating in the Natural Sciences Tripos, he attached himself to Trinity Hall, and for many years devoted himself to the interests of the students as a private tutor. From the time of taking his first degree up to the date of his death he was identified with the University Chemical Laboratory, where his success as a teacher, first as Demonstrator and later as University lecturer, will long be gratefully remembered.

Shortly after graduating, Dootson became interested in the chemistry of citrazinic acid, a subject on which his teacher, the late W. J. Sell, had published several memoirs. A paper published by Sell and Dootson on the action of phosphorus pentachloride on citrazinic acid in 1897 led to a systematic study of the chlorine derivatives of pyridine. The results of these investigations were published at frequent intervals in the *Journal* between 1898 and 1903. Dootson also published a paper on the "Halogen Derivatives of Acetonedicarboxylic Acid" (*J.*, 1899, 75, 169), and in another paper, entitled "Condensation of Methyl Acetonedicarboxylate. Constitution of Orcinoltricarboxylic Esters" (*J.*, 1900, 77, 1196), he demonstrated a very simple method for transforming an aliphatic into a benzenoid compound.

After 1903, Dootson's administrative duties in the laboratory increased considerably and he was of necessity drawn away from research. During the period of the War, however, he was actively occupied with experimental preparative work on various substances of national importance. His last memoir, entitled "A Note on Thermal Diffusion" (*Phil. Mag.*, 1917, 33, 248), was published jointly with Dr. S. Chapman.

To past and present generations of Cambridge students, however, the most enduring memory of Dootson will be that of an attractive



and successful teacher of the more elementary branches of chemistry. His admirable capacity for organisation made him a valuable help to his Professor and a very kindly friend to other members of the Departmental Staff. Dootson was a man of many interests: not only was he essentially a "well-read man," but he developed his appreciation of art in a more practical way as a very successful amateur oil painter.

He died, as he would have wished, in harness, after a very short illness. Among the many tributes to his memory, the writer ventures to quote from a letter written by an eminent Member of the Faculty of Medicine to Mrs. Dootson. "... I should like to add my appreciation of Dr. Dootson's work as a teacher. He was a friend to every student, and every student valued his kindly and unsparing help."

A. J. BERRY.

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### HENRY JOHN HORSTMAN FENTON.

BORN 1854; DIED JANUARY 13TH, 1929.

HENRY JOHN HORSTMAN FENTON was born at Ealing in 1854. He received his earlier education at Magdalen College School, Oxford, and afterwards went to King's College, London, where he studied chemistry under Bloxam. During the time that Fenton was at King's College the Clothworkers' Company instituted an exhibition in physical science tenable for three years by a non-collegiate student at Cambridge. Fenton applied successfully for this exhibition and, in accordance with its conditions, entered the University of Cambridge in the Lent Term, 1875. In his first year at Cambridge he gained an entrance scholarship at Christ's College, where he was admitted in May 1876. He was then 22 and thus older than the majority of undergraduates. His chemical knowledge and experience were also greatly in advance of those of men of the same university standing, and while still an undergraduate he was made an assistant demonstrator by Professor Liveing. He had a very independent spirit, and it was therefore perhaps not unnatural that he chafed at the discipline then imposed on members of the University *in statu pupillari* and not infrequently came into conflict with University and College authorities. In fact to the end he cherished a certain antagonistic attitude towards university authority. He took the Natural Sciences Tripos in 1877—it was at that time not divided into two parts—and was placed in the First Class along with, amongst others, Adam Sedgwick, the zoologist, F. O. Bowen, afterwards Professor of Botany at Glasgow, and Alex. Hill, sometime Master of Downing.

On the resignation of the then University Demonstrator of Chemistry, John Wale Hicks, of Sidney Sussex, afterwards Bishop of Bloemfontein, W. J. Sell was appointed to succeed him and an "Additional Demonstratorship of Chemistry" was instituted by the University and the post was assigned to Fenton.

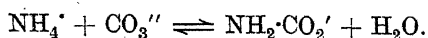
The University Department of Chemistry was then accommodated in a building since removed, which stood on the southern part of the east side of the Old Botanic Garden site and afterwards served as part of the Pathological Laboratory.

Several of the Colleges had their own chemical laboratories and these were run in competition with the University laboratory. This competition continued for many years after the erection in 1887 of the new University Chemical Laboratory facing Pembroke Street, though in an ever-lessening degree as the college laboratories one by one were given up. The greater part of the teaching in the University Laboratory was carried on by Sell and Fenton and in spite of their different temperaments the two men worked together in harmony until their association was terminated by the death of Sell in 1915.

Fenton's lectures were for many years an outstanding feature in the instruction given in the University Laboratory. He took immense pains in their preparation and although in lecturing he affected an air of indifference and a somewhat indolent manner, actually he delivered them with very great care, and he was extraordinarily successful in stimulating the interest of the abler men. He scrupulously avoided dogmatism. He endeavoured, so far as possible, to present each subject as a debatable question on which there were diverse views to be discussed, to balance the evidence for and against every inference, and to induce his hearers to use their own judgment and draw their own conclusions. The value of his lectures was greatly enhanced by the informal discussions which he encouraged: at the close of every lecture a number of eager young men would come down to the lecture table and engage with him in discussion, often prolonged, of the subjects in which he had aroused their interest. Those who brought their difficulties to him found him unexpectedly sympathetic, and he would deal exceedingly gently with one who asked a thoughtless or an ill-considered question.

The course of experimental work in general and physical chemistry which he devised to illustrate his lectures was very carefully thought out, and during the 'eighties, and even later, the type of laboratory work being done by his class was probably unique. Although his chief interest always seemed to be in general and physical chemistry, the greater part of his original work was carried out in organic

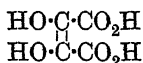
chemistry. His earlier work consisted of a series of investigations on the action of hypochlorites on urea and related compounds. A pupil of his (Mr. Street), wishing to estimate urea, happened to use, instead of sodium hypobromite, a strongly alkaline solution of sodium hypochlorite and found that only half the expected quantity of nitrogen was evolved. Fenton followed up this observation and discovered that the missing half of the nitrogen was present in the solution as sodium cyanate. He gave an explanation of the phenomenon a few years later. At the same meeting of the Chemical Society (June 20th, 1895) at which Walker and Hambly communicated their well-known experiments on the transformation of ammonium cyanate into urea Fenton read a paper giving an account of experiments he had been making on the same subject, using the action of sodium hypobromite to measure the rate of change. Finding that the transformation of the ammonium cyanate was never complete, he inferred that ammonium cyanate and urea were in tautomeric equilibrium and concluded that, whilst the more reactive hypobromite attacked both the urea and the ammonium cyanate (liberating all the nitrogen from the former and that present as ammonium from the latter), the hypochlorite attacked the ammonium cyanate only and thereby disturbed the equilibrium of the system so that the whole of the urea was finally converted into nitrogen and sodium cyanate. In other papers he showed that hypochlorites and hypobromites liberated different amounts of nitrogen from several nitrogenous compounds and in this manner he proved that ammonium carbonate in presence of water was in equilibrium with a small proportion of ammonium carbamate :



What is probably to be regarded as his most important work is that connected with the discovery and investigation of dihydroxy-maleic acid. It extended over many years, for the initial observation from which it grew was made during his first year as an undergraduate at Cambridge. The story current in the laboratory in later years was that a fellow student, amusing himself by mixing reagents at random, chanced to obtain a violet coloration, which he showed to Fenton. Fenton was keenly interested in the observation, and he found out the essential reagents which were concerned in the production of the colour, namely, tartaric acid, a ferrous salt, hydrogen peroxide, and excess of caustic alkali. He reported the discovery in a letter to the *Chemical News*, entitled "On a New Reaction of Tartaric Acid" and dated Christ's College, Cambridge, April 25th, 1876. He was at first disposed to regard the colour as being due to the production of a ferrate, but a few years later (in

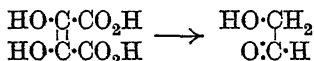
1881) he published a second letter in the *Chemical News* in which he showed that the colour arose from an iron derivative of an oxidation product of tartaric acid, since the colourless solution obtained after removal of the iron gave the colour again on the addition of a ferrous or ferric salt.

After several years he took up the problem again, and in 1894 he discovered how the new oxidation product could be isolated—it could be salted out from the reaction mixture by the addition of fuming sulphuric acid—and in a series of papers extending over the years 1894 to 1902 he described its reactions and relationships. It had the formula  $C_4H_4O_6$ ; its formation from tartaric acid thus involved only the loss of two atomic proportions of hydrogen. It was a dibasic dihydroxy-acid; it showed no ketonic reactions; it could be reduced to racemic acid and oxidised to dihydroxytartaric acid. It was therefore either dihydroxyfumaric acid or dihydroxymaleic acid. It readily gave a diacetyl cyclic anhydride with acetyl chloride and was transformed into an isomeric acid by hydrobromic acid. Fenton therefore regarded it as dihydroxymaleic acid :

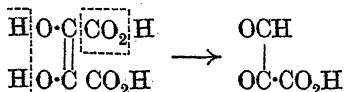


Its production from *d*-tartaric acid thus involves the *trans*-elimination of the two hydrogen atoms lost, and its reduction to racemic acid the *trans*-addition of hydrogen.

The most interesting reaction of the new acid was perhaps that brought about by heating with water. Two molecules of carbon dioxide were eliminated and glycollaldehyde was formed :



On re-examining this reaction with H. Jackson, he obtained the resulting glycollaldehyde in a bimolecular crystalline form. It had a sweet taste (it could be regarded as the simplest sugar) and Fenton showed subsequently that it could be degraded by Wohl's method to formaldehyde. With Ryffel, he showed that dihydroxymaleic acid could be oxidised to mesoxalic semialdehyde, a compound of considerable interest on account of its close relationship to the hypothetical trihydroxyacrylic acid of which uric acid is the diureide.



Nevertheless attempts to synthesise uric acid by condensing this compound with urea yielded only glycouril and carbon dioxide.

Further investigations showed that the new reagent—hydrogen peroxide in conjunction with ferrous salts—which acted on tartaric acid in so characteristic a manner, constituted a specific and valuable oxidant for certain classes of compounds. With H. Jackson, Fenton showed that di- or poly-hydroxy-alcohols with vicinal hydroxy-groups were smoothly and rapidly oxidised to hydroxy-aldehydes; for instance, glycol gave glycollaldehyde, glycerol glyceraldehyde, erythritol erythrose, and mannitol mannose. Monohydric alcohols, however, were not attacked. With H. O. Jones, he examined the effect of the new reagent on acids.  $\alpha$ -Hydroxy-acids were oxidised rapidly and with evident heat-evolution to the corresponding keto-acids; acids of other classes were unaffected. Thus glycollic acid was shown to be oxidised to glyoxylic acid, lactic acid to pyruvic acid, tartronic acid to mesoxalic acid, and glyceric acid to hydroxypyruvic acid, whilst from malic acid there was formed the previously unknown free oxalacetic acid. Fenton and Jones examined the reactions of this acid in some detail and among other observations found that its phenylhydrazone, heated with water, decomposed in two ways, either losing carbon dioxide to give pyruvic acid phenylhydrazone, or undergoing dehydration to a pyrazolone derivative. The relative proportion of these products depended on the hydrogen-ion concentration of the solution, and on this fact an approximate method of comparing the strengths of acids could be based.

The observation that dihydroxymaleic acid was converted into its diethyl ester by the action of an ethereal solution of hydrogen bromide led him to examine the action of this mixture on compounds of other classes. With Miss M. M. Gostling, he found that various carbohydrates, in particular fructose, gave a purple colour when dissolved in ether and treated with hydrogen bromide, and this proved to be due to an oxonium salt of a yellow crystalline compound which could be thus obtained in considerable quantity and was shown to be  $\omega$ -bromomethylfurfuraldehyde.

Among other observations of interest which he made may be mentioned the reduction of carbonic acid by magnesium to formaldehyde and the formation of a crystalline explosive compound of formaldehyde and hydrogen peroxide of the composition  $C_2H_6O_4$  and the probable constitution  $HO\cdot CH_2\cdot O\cdot O\cdot CH_2\cdot OH$ .

Fenton was gifted with keen powers of observation and acuteness of interpretation and the whole of his experimental work is marked by its elegance.

Of his books, those best known are his "Notes on Qualitative Analysis," which was based originally on a small book published by Liveing, but was greatly expanded in successive editions, and his

"Outlines of Chemistry." He was elected into the Royal Society in 1899, and served on the Council of that body from 1913 until 1916. He was made an honorary fellow of his College in 1911.

He was naturally a shy man and was exceedingly sensitive to chaff or criticism; he endeavoured to conceal his shyness by assuming a certain *hauteur* which tended to repel some of those who would have sought his friendship. He had a very strong sense of fairness, but his pertinacity in defending views in which he was in a minority of one sometimes made him a difficult member of University bodies. He married in 1892, Edith, daughter of George Ferguson of Richmond. He left no children. He gave up his lectureship in 1924 and went to live at Hove, but the last years of his life were greatly clouded by illness. He died in a nursing home in London on January 13, 1929, at the age of 74.

W. H. M.

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### HENRY WILSON HAKE.

BORN DECEMBER 17TH, 1851; DIED JANUARY 18TH, 1930.

H. WILSON HAKE, who died in January aged 78, was the last surviving son of Dr. Thomas Gordon Hake, author of "Madeline," "Parables and Tales," and other poetic works.

He was educated privately up to 1872 and then went to the University of Giessen, where he took his Ph.D. (1875), and subsequently to Bonn for a short post-graduate course, studying under Professors Will and Kekulé. He formed a close friendship with the younger Will. After travelling for some time with his father in Italy, he returned to England and became an assistant to Thudichum, with whom the writer had for some two years previous been associated in researches chiefly concerning the chemistry of brain-matter.

For some years we were intimately acquainted and during that time we communicated a joint note to the Chemical Society on "Some New Reactions in Organic Chemistry," which was published with a supplemental note in the *Pharmaceutical Journal* of May 12th, 1877. We also contributed to the *Quarterly Journal of Science* (January, 1877) a joint critical essay on "Physiology and its Chemistry at Home and Abroad."

Hake became acquainted with my old friend Thomas Farries and upon leaving Thudichum he took charge of the laboratory of his firm (Messrs. Burgoyne, Burbidge, Cyriax, and Farries) for about one year: he was then appointed Lecturer on Chemistry at Queenswood College, Stockbridge, Hants (1879—1885). In 1885 he became Assistant Lecturer on Chemistry at

Westminster Hospital Medical School and assisted Dr. A. Dupré in his analytical and consulting practice; he also collaborated with him in the production of a "Manual of Inorganic Chemistry," published in 1886. In 1897 he succeeded Dupré as Lecturer on Chemistry and Toxicology and although the Chemistry Department was discontinued in about 1907 he continued to coach students for the D.P.H. degree and lectured on Toxicology up to June, 1929—some six months prior to his decease.

Hake was an examiner in Chemistry for the Civil Service Commission from 1894—about 1918, and for the Royal College of Physicians from 1898—1902: during the period 1901—about 1917 he was Lecturer on Toxicology at the London (Royal Free) Hospital School of Medicine for Women and from about 1922—1926 he served as Examiner on Public Health to the Conjoint Board of Physicians and Surgeons. He also served for many years as Gas Examiner to the Wandsworth Borough Council. In addition to his other activities he specialised in the analyses of mineral and ordinary waters and did a good deal of consulting work on poisons, drugs, medicines, etc. Among his publications may be mentioned a joint paper with Thudichum on "The Estimation of Hydrogen occluded by Copper, with Special Reference to Organic Analysis" (J., 1876); a joint paper with A. Dupré on "The Estimation of Organic Carbon in Air" (J., 1881); "A Preliminary Note on the Absorption of Moisture by Deliquescent Salts" (P., 1896); a note on "Further Experiments on the Absorption of Moisture by Deliquescent Substances" (P., 1897); an article entitled "Chemistry and Medicine" (*Westminster Hospital Reports*, Vol. 3, 1887); a further paper on the same subject (*ibid.*, Vol. 5); a joint paper with Dr. William Murrell on "Green, Blue, Magenta, and other coloured Urines" (*Edinburgh Med. J.*, 1906); a joint paper with Dr. S. Monckton Copeman entitled "A Study of the Variations in the Secretion of Hydrochloric Acid in the Gastric Contents of Mice and Rats as compared with the Human Subject, in Cancer" (*Proc. Roy. Soc.*, 1908, B, Vol. 80); "Report on Ferro-Silicon with Special Reference to the Poisonous Gases evolved" (extracted from supplement to the 38th Annual Report, Local Government Board, 1908—1909; Cd. 4958); joint Report with Dr. S. Monckton Copeman and S. R. Bennett, M.A., on the "Nature, Uses, and Manufacture of Ferrochrome and other Ferro-Alloys" (Reports, Local Government Board, New Series, No. 93, 1911); "The Action of Chlorine on the Blood" (*Lancet*, July 10th, 1915); and "Some Problems in Toxicology" (Post-graduate Lecture at the Westminster Hospital, 1924).

Hake became a Fellow of the Chemical Society in 1876, and a

Fellow of the Institute of Chemistry in 1878 and served on the Council (1901—1904). As will be obvious from what has been written above, he was specially interested in Toxicology and almost up to the time of his death he was occupied in the preparation of notes with a view to the publication of a text-book on that subject.

In 1890 Hake married Miss Mabel Mann (youngest daughter of Richard Mann of Bromley, Kent), who died in 1924, leaving as issue one son (the present Director of the National Portrait Gallery) and two daughters. Hake took the greatest possible interest in the education of his children. He was a good lecturer and teacher and had a great love of nature. Highly cultivated, of charming manners and retiring disposition, he was a lovable man and it is a matter of great regret to me as an old friend that I was able to see so little of him since our early intimate association.

CHARLES T. KINGZETT.

### WILLIAM WALKER JAMES NICOL.

BORN JUNE 27TH, 1855; DIED MARCH 19TH, 1929.

WILLIAM WALKER JAMES NICOL, the only son of William Walker Nicol and Marianne Ballantyne Nicol, both belonging to old Border families, and the nephew of James Nicol, Professor of Natural History, who elucidated the nature of the rock formation of the North-west Highlands, was born in Edinburgh in 1855. He was educated first in England, and later at the Edinburgh Academy, where he was a contemporary of the late Lord Haldane; in 1872 he proceeded to the Edinburgh University, where he took the M.A. degree. Attracted by chemistry, he turned his special studies in this direction in Professor Crum Brown's laboratory, and gained the medal of the year and the Hope Prize Scholarship, taking also the B.Sc. and finally the D.Sc. degree. After working at Berlin University under Professor A. W. Hofmann, he returned for a short time to Edinburgh University as demonstrator, and in 1876 was appointed lecturer at the newly founded University College, Bristol, now the University of Bristol. In 1880, Mason College, Birmingham, now the University of Birmingham, was founded, and in 1881, with William Augustus Tilden as professor, Nicol joined the staff as lecturer in chemistry: he retained this post until his retirement in 1894, following on Tilden's removal to the Royal College of Science, South Kensington.

During this period of 18 years Nicol proved himself a very successful lecturer and teacher. As a lecturer he was clear and logical and his lectures were appreciated, not only by his students, but by



wider and more popular audiences to whom he gave numerous lectures in the West of England and the Midlands, partly as University Extension Lectures and partly under the Gilchrist Trustees. As a teacher in the laboratory, he was indefatigable in his individual attention to his students, being at all times both able and willing to help them in their difficulties.

At this period, especially in newly founded Chemical Departments, the time of the members of the staff taken up in lecturing and in the daily work of the laboratory was frequently so great as to leave but little for research, and the equipment and apparatus available were often very limited. Nicol, however, always devoted as much time as could be spared from other duties to research work : he was greatly helped in this respect by the possession of an exceptionally good mechanical aptitude and an unusually skilful manipulative capacity, which enabled him to construct his own apparatus, whether of wood, metal, or glass, thus minimising the difficulties which many would have experienced owing to lack of equipment. At the outset, while in Berlin and later in Edinburgh, he carried out short investigations in organic chemistry, but the bent of his mind was much more towards inorganic and physical chemistry, and it was especially in this direction that he turned during his stay in Birmingham.

The particular problem which attracted Nicol was that of "solution," and from 1882 to 1894 he carried out a long series of investigations on the physical constants of salt solutions, and especially of their molecular volumes, these being ascertained with the high degree of accuracy characteristic of his work. In the controversies of the period, which just preceded the rapid development of physical chemistry in the 'nineties, he took a considerable part as an opponent of the "hydrate" theory of solution : he also acted as Secretary of the British Association Committee on Solution. He was a very expert photographer, and worked out the "Kallitype" printing process, in which silver nitrate and ferric salts were employed.

After his retirement from active teaching work in 1894, although he continued his chemical investigations for a time, Nicol's interests tended more and more to the fulfilment of the mechanical bent of his versatile inventive mind. One outlet of this, joined with his love of natural scenery and of the open air, was found in caravanning in the wildest parts of the Scottish Highlands, and along the narrowest and most difficult of roads in various types of caravan, first with a horse and later with the motor as tractor, the caravans, full of ingenious contrivances, being built and fitted entirely by himself.

Externally rather quiet and reserved, Nicol felt no great inclination for large meetings or social functions, but those who were regularly brought into contact with him soon learned how thin was this external layer, and beneath it soon recognised his high-minded sense of honour, his innate courtesy, and his intellectual capacity, and that these were combined with a great personal hospitality and a strong sense of dry humour. To those intimate with him he was to the end, even when opportunities of meeting became rare, a friend who continued always the same.

During most of his life Nicol enjoyed very robust health, and it was a legitimate source of pride to him that throughout the whole time he spent in Birmingham he was never for a single day absent from his work through illness. During the last year or so, however, his health failed, and he died in his 74th year on March 19th, 1929. He leaves a widow and one daughter, Dr. E. A. Traquair Nicol, who, after taking the B.A. degree at Cambridge and the Ph.D. at Edinburgh, is now carrying out zoological research in the laboratory of the latter University.

H. G. C.

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### SAMUEL RIDEAL.

BORN, 1863; DIED NOVEMBER 13TH, 1929.

DR. SAMUEL RIDEAL, who died on November 13th last at the age of sixty-six, had been a Fellow of the Society since 1882, and for the greater part of his life was a familiar figure at its meetings and at those of kindred societies.

Rideal was born in 1863, being the son of Mr. John Rideal of Sydenham, and was educated at Dulwich College and at the Royal School of Mines, whence he migrated to University College, London; there he completed his degree course and acted for several years as an assistant teacher, first under Professor Williamson and later under Sir William Ramsay. He took Chemical Honours in his B.Sc. Degree and only two years later was awarded the Doctorate at the very early age of twenty-three—a considerable achievement in the days when the D.Sc. was awarded, not, as later, for original work, but as the result of an examination of almost encyclopædic range demanding, not only a severe course of intense reading, but also the possession of an exceptionally retentive memory. His investigational work in chemistry, which was varied and continuous and gave him a wide reputation, came later.

In 1886, however, he contributed to the *Transactions* of our Society by a paper on the "Action of Ammonia on Chromyl Dichloride" (J., 1886, 49, 367), and in 1889 a paper on the "Action of Ammonia on Tungsten Compounds" (J., 1889, 55, 41). But he

had already contributed some original observations on analytical methods to the *Chemical News* and a paper on "Isodimorphism" (in relation to the specific volumes of arsenic and antimony trioxides in their octahedral and prismatic forms) to the *Berichte* of the German Chemical Society (1886, 19, 589).

In 1889, after having received the honour of election as a Fellow of his College, Rideal was appointed Lecturer on Chemistry in the Medical School of St. George's Hospital; and soon after, on his appointment as Public Analyst for Chelsea, he established himself as a chemical consultant at Westminster.

A communication from him to the German Chemical Society on "Organic Boron Compounds," dealing with the action of boron halides on ammonia and on organic bases, was published in the *Berichte* (1889, 22, 992). He gradually, however, turned his attention mainly to problems of a technical nature, his first memorable contribution in this direction being a paper, with S. G. Rosenblum as co-author, on the "Estimation of Chromium in Chrome Iron Ore, Ferro-chromium, and Chrome Steel," in which were communicated the results of a searching investigation into the method of fusion with sodium peroxide which had been put forward by Hempel in 1893 and adapted for quantitative purposes by Dr. John Clark as described in a communication by the latter to our own Society (J., 1893, 63, 1079): the subject was further pursued by Rideal and Rosenblum in a paper in the *Chemical News* (1896, 73, 1), to which was appended a very complete bibliography of other work on the same process.

Rideal's attention, however, became concentrated on matters connected with sanitation, mainly those bearing upon water supplies and, more especially, upon the disposal and purification of sewage and sewage effluents; on this subject he became a generally acknowledged authority, his assistance being constantly requisitioned by engineers and by local authorities, and he was frequently called upon to give evidence before Royal Commissions, Departmental Committees, and Local Government enquiries relating to sewage disposal or public water supplies.

Rideal also gave a good deal of attention to disinfectants and his name has for many years been familiar in connexion with the Rideal-Walker method for assessing the value of disinfectants on the basis of comparison with pure phenol by ascertaining their relative effect on cultivations of *Bacillus typhosus*.

He was the author of a book entitled "An Introduction to the Study of Disinfection and Disinfectants," first published in 1895, with subsequent editions in 1898 and 1904, which work, however, was superseded by a later edition by himself and his son, Dr. Eric

K. Rideal, on "Chemical Disinfection and Sterilisation" published in 1921.

He was also the author of a book on "Sewage and the Bacterial Purification of Sewage," first published in 1900 and re-published in 1901 and 1906; and in 1914, again jointly with his son, he published what has come to be regarded as a standard work on "Water Supplies, their Purification, Filtration, and Sterilisation."

The application of electrolytic chlorine to sewage purification and deodorisation engaged Rideal's attention over several years, and he was the author of two papers on the subject (*J. Roy. Sanit. Inst.*, 1905, 26, 378; *J. Soc. Chem. Ind.*, 1909, 215).

He was also the author of a book on "Glue and Glue Testing"; and made several communications to the Society of Public Analysts recorded from time to time in the *Analyst*. Amongst these were papers on "The Sulphuric Acid Hydrolysis of Butter-Fats" (1893, 18, 165); on "Formalin as a Milk-Preservative" (1895, 20, 157); on "Determination of Dissolved Oxygen in Waters in Presence of Nitrites and of Organic Matter" (1901, 26, 141); (jointly with H. G. Harrison) on the "Polenske Method for the Detection of Cocoanut Oil in Butter" (1906, 31, 254); (jointly with W. T. Burgess) on the "New Standards for Sewage Effluents" (1909, 34, 193); (jointly with L. H. D. Acland) on "Examination of the Oils from Manihot Ceara and Funtumia Elastica and a Comparison of their Properties with those of Linseed and Hevea Oils" (1913, 38, 259).

Rideal was chosen as Cantor Lecturer to the Royal Society of Arts in 1902, taking as his subject "Water Purification" (*J. Soc. Arts*, 1902, 50, 717, 729, 741, 755).

He was President of the Association of Sewage Works Managers in 1902, and President of the Society of Public Analysts in 1918; and he served a period as Examiner in Chemistry to the Royal Colleges of Physicians and Surgeons.

During recent years Rideal's health gradually failed, compelling him to give up—it was hoped only for a time—active work, and on medical advice he sought change of scene abroad; but the hoped-for recovery did not ensue and he died with unexpected suddenness in South Africa, leaving a widow (Lilla, daughter of the late Samuel Keightley, of Bangor, Co. Down), one daughter, and three sons, including Dr. Eric K. Rideal, Owen Jones Lecturer in Physical Chemistry in the University of Cambridge, already referred to in connexion with two books of which, with his father, he was joint author.

The writer deplores the termination of an intimate personal friendship which had lasted unbroken through more than forty years.

BERNARD DYER.

## SAMUEL BARNETT SCHRYVER.

BORN, 1869; DIED AUGUST 21st, 1929.

SAMUEL BARNETT SCHRYVER was born in London in 1869 and was educated at University College School, University College, and the University of Leipzig, where he graduated Ph.D. After his return to England he was appointed in 1893 Demonstrator in Chemistry under Campbell Brown at University College, Liverpool, where he remained until 1897. Early in 1898 he joined the staff of the Wellcome Research Laboratory and retained this position until March 1901, when he was appointed Lecturer in Physiological Chemistry at University College, London. Up to this time he had been engaged in research on a variety of subjects in Organic Chemistry, but here for the first time he came into direct contact with biochemical problems and henceforward until his death he was continuously engaged in biochemical and physiological research. He left University College in 1907, on his appointment as Physiological Chemist to the Research Institute of the Cancer Hospital, and in 1913 joined the Staff of the Imperial College of Science at South Kensington as Assistant Professor, becoming full Professor of Biochemistry in 1920. Schryver was elected to the Fellowship of the Royal Society in 1928. He died on August 21st, 1929 after an illness of several months' duration.

Trained as an organic chemist, Schryver developed into a biochemist whose chief interest lay in the chemical and physical behaviour of the proteins and other colloidal constituents of the cell. Gifted with a fertile imagination, he was never lacking in ideas for new lines of research, many of which he himself began to develop. He leaves behind him a band of workers trained in his laboratory, many of whom are continuing the work commenced under his inspiration.

In 1910 Schryver married Miss E. Davies, who, with their two daughters, survives him.

Schryver's first paper (1890) was published in conjunction with Norman Collie, under whom he studied, on the effect of heat on quaternary ammonium compounds and the nature of the tertiary amine thus formed when the radicals of the quaternary compound were varied. This led to an attempt (1891) to prepare stereoisomeric compounds of the quaternary ammonium salt type (methyldiethyl-isoamylammonium iodide). Certain differences in crystallisation (probably due to dimorphism) were regarded as possibly due to the effect of asymmetry of the nitrogen atom.

At Liverpool he commenced the study of the oxidation of oil of turpentine, from which he obtained a new acid (terpylonic acid).

The heptolactone formed by distillation of terpenylic acid and an isomeric lactone were synthesised and their constitutions thus established. He next turned to researches on the derivatives of camphor, effecting the synthesis of an isomeride of camphoric acid and studying the oxidation products of lauronic acid.

From the Wellcome Research Laboratories he published papers on acid phenyl salts of dibasic acids, which were obtained by acting on the anhydrides of such dibasic acids as camphoric, succinic and phthalic acids with the sodium salt of a phenol. Here too he commenced (with F. H. Lees) an investigation on morphine and published two papers on this subject, dealing with *iso*- and  $\beta$ -*iso*-morphine. He also devised a method for the estimation of phenols, depending on the production of ammonia from sodamide by the action of the dry phenol dissolved in anhydrous benzene.

At University College, in the course of unsuccessful attempts to effect the synthesis of proteins from peptones in presence of intestinal mucous membrane, his attention was drawn to the phenomenon of autolysis, which was investigated (partly in collaboration with Miss Lane Claypon) in some detail (1904, 1905, 1906). He finally reached the conclusion that the autolysis of the organs *in vivo* was regulated by chemical means and that the normal supply of nitrogenous food yielded by its breakdown sufficient ammonia to prevent the tissues from becoming acid and then undergoing autolysis.

Whilst at University College he also made experiments (with Hamill) on the excretion of nitrogen by normal individuals, finding that it corresponded to a daily intake of 93 g. of protein. In the course of investigations carried out for the Local Government Board he devised new and delicate methods for the detection of tin and of formaldehyde in foodstuffs. The application of the latter test enabled him to show the production of formaldehyde when chlorophyll was exposed to sunlight in the presence of moist carbon dioxide.

At the Cancer Hospital he carried out with Dr. C. Singer investigations on the gastric juice in malignant and non-malignant diseases of the stomach and duodenum (1913) in which chemical methods (*e.g.*, determination of the peptic index and of the ratio of acid combined with amino-acids to total nitrogen) were applied to diagnosis. To the last he retained an intense interest in the biochemistry of cancer. Here he also began work on the state of aggregation of matter, which led directly to the study of clot formation, the results of which formed the subject of a series of seven papers published between 1910 and 1919. These included useful

studies of the relation between the viscosity and surface tension of salt solutions and the effect of these salts on clotting and gel formation and an intensive examination of the clotting of milk by rennin, in the course of which he showed that caseinogen is converted into a less soluble "metacaseinogen" by treatment with hot water but that this substance differs in properties from the casein produced by rennin. He also (1912) made a study of the unconjugated acids of ox-bile and devised a method of separation of cholalic, choleic and deoxycholeic acids, depending on the solubilities of their magnesium and barium salts.

Schryver's deep interest in gel formation was maintained in the investigations which he carried out at the Imperial College. These followed two main lines. In the first place he attacked the constituents of plant cells, preparing and studying the proteins of leaves and also studying the cell wall, from which he isolated the pectins and hemicelluloses which take a part in its structure. He came to the conclusion that pectinogen is a trimethyl ester of pectic acid combined loosely with metallic ions, such as  $\text{Ca}^{++}$ , and that pectic acid and the hemicelluloses, a number of which were isolated from various materials, were both complexes of "uronic acids" and sugars, as suggested by Ehrlich and Ling. For such complexes he suggested the name "polyuronides." Lignification of tissue he found (1928) to be accompanied by the disappearance of pectins.

The second group of researches arose from work done under the auspices of the Adhesives Research Committee, of which he was made a member. This Committee was appointed by the Department of Scientific and Industrial Research in 1919 to take over the work of the Adhesives Committee originally appointed by the Conjoint Board of Scientific Societies in the latter part of 1917. This work, carried out largely in conjunction with his students, resulted in two series of papers, on the preparation, purification and properties of gelatin and on the separation of the products of protein hydrolysis. Many of these results are also contained in the First and Second Reports of the Adhesives Research Committee (1922, 1926): a Third Report, also containing much of his work, is in course of preparation.

The formation of gelatin from its precursors collagen and ossein was studied from the physico-chemical standpoint. Elaborate attempts were made to "purify" gelatin and obtain a material which could be regarded as a chemical entity, but without complete success. He found that a large degree of purification could be effected by electrolysis and by flocculation in an electric field. The resulting material, however, is probably always to some degree

contaminated by products formed by the action of water, which produces an irreversible change, measurable in a few hours, even at 37°. Such "purified" gelatin is almost insoluble in water at 15° and is very similar in properties to the globulins, from which it differs by its power of readily forming gels when dispersed in acids, alkalis or salts.

In the course of these researches the important observation was made (Knaggs, 1923) that the composition of gelatin was not constant, but varied with the treatment to which either the gelatin itself or its precursor had been subjected. This was detected by a variation in the percentage of the total nitrogen of the hydrolysis products which were precipitated by phosphotungstic acid (diamino-nitrogen). For instance, the hydrolysis products of gelatin from a precursor which had been treated with dilute alkali yielded 29.5%, whereas those of gelatin from the same precursor treated with dilute acid gave only 26.0% of diamino-nitrogen; gelatin itself showed similar changes, but of even greater magnitude.

These results have been criticised by Daft, working in the Carlsberg Laboratory, but the criticism has been refuted by Thimann (1930), one of Schryver's students, who has explained the apparent divergence of experimental results. The investigation of this phenomenon led to the work on the separation of the products of protein hydrolysis. In this pioneering work, which must be regarded as preliminary and awaiting further extension and confirmation, Schryver developed a method of separation of the products of protein hydrolysis which depended on the use of Siegfried's barium carbamate compounds of the amino-acids. In this way he obtained from the hydrolysis products of isinglass (and of edestin, but not of caseinogen or egg-albumin) hydroxylysine, in the form of a barium carbamate soluble in 70% alcohol but insoluble in cold water, whilst from the glutelin which he isolated from oats he obtained two new aminohydroxy-acids, aminohydroxybutyric acid, which forms an insoluble copper salt, and aminohydroxyvaleric acid, which forms a soluble copper salt.

In addition to this he obtained a new eight-carbon acid,  $C_8H_{15}O_3N_3$ , which he termed protoctin, from the phosphotungstic acid precipitate obtained from the soluble carbamate from glutelin and the protein of castor bean. Finally, *DL*-lysine was obtained from gelatin which had been treated with acid before being hydrolysed and to this the increased percentage of diamino-nitrogen found in such gelatin was traced. No clue was, however, found to the origin of this extra lysine.

Schryver (with Chibnall) also initiated an investigation into the



proteins of leaves, which has been continued with great success by Chibnall. He, moreover, isolated a crystalline substance,  $C_3H_8O_4$ , from cabbage leaves, which he regarded as a disaccharide derived from glycollaldehyde and formaldehyde.

From 1918 up to the time of his death he was also engaged in researches on the autolysis and nutrition of yeast in connexion with the Research Scheme of the Institute of Brewing. The interesting fact was observed that when yeast is washed it is only autolysed very slowly, and much work was expended in endeavouring to trace the presumed agent removed by washing, but without any definite result. The work on yeast nutrition had only reached a preliminary stage at the time of Schryver's death.

He was the author of two books. "An Introduction to the Study of Biological Chemistry" (1918) provided a general introduction to Organic Chemistry, followed by special chapters on the chief chemical constituents of the animal body (fats and lipoids, carbohydrates, proteins); the methods employed for the investigation of chemical changes within the animal organism (metabolism, total and intermediary); and the chemical processes taking place in plants (including enzyme actions). This was also the plan he adopted in his lectures. He also contributed in 1909 an early volume to Longman's Series of Monographs on Biochemistry on the general characteristics of the proteins.

A. HARDEN.

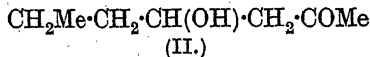
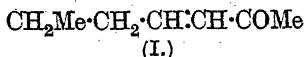
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## CXII.—*The Isomerism of the Butylideneacetones.*

By EUSTACE NEVILL ECCOTT and REGINALD PATRICK Linstead.

THE movement of the double bond in unsaturated ketones containing an unbranched carbon chain has been but little investigated, although a considerable number of allied substances with a  $\beta$ -substituent, of the type of mesityl oxide, have been studied. The only direct investigation of the normal ketones is that of Blaise (*Bull. Soc. chim.*, 1905, **33**, 40), who showed that allyl alkyl ketones were readily converted into their  $\Delta^{\alpha}$ -propenyl isomerides by both acid and alkaline catalysts, a process involving an apparently irreversible movement of the double bond from the  $\beta\gamma$ - to the  $\alpha\beta$ -position. In attempting to correlate these earlier observations with the recent work on three-carbon tautomerism, we were led to examine the related pentenyl methyl ketones. At the outset, however, certain unexpected features were encountered in the preparation of the  $\alpha\beta$ -ketone, *n*-butylideneacetone, from *n*-butaldehyde and acetone, and this reaction was systematically reinvestigated.

The condensation of aldehydes with ketones, and more particularly acetone, originally examined by Schmidt and by Claisen and extended to aliphatic aldehydes by Barbier and Bouveault (*Compt. rend.*, 1895, **120**, 1270), was first applied to *n*-butaldehyde by Weizmann and Garrard (J., 1920, **117**, 324), who isolated an unsaturated ketone to which the formula (I) was given.



Under milder conditions, Grignard and Dubien (*Ann. Chim.*, 1924, **2**, 287) were able to isolate the ketol (II), a type of compound already recognised as an intermediate in such reactions (Claisen, *Ber.*, 1892, **25**, 3164; Francke and Kohn, *Monatsh.*, 1899, **20**, 876). Dehydration of (II) with iodine yielded a ketone (semicarbazone, m. p. 118°) identical with that of Weizmann and Garrard.

As a result of a large number of experiments on this condensation, using aqueous alkali as catalyst, we find that under most conditions mixtures of unsaturated ketones and ketol are produced. It has, however, been possible to develop one method by which an unsaturated ketone is obtained direct in a state of considerable purity, and one, similar to that of Grignard and Dubien, for preparing the pure ketol (II). Dehydration of this has been investigated with iodine, acetic anhydride, and anhydrous oxalic acid, all of which produce an unsaturated ketone giving a semicarbazone melting at 124° after repeated crystallisation, the purest material being that obtained with oxalic acid as dehydrating agent. The butylideneacetone of previous workers is believed to be essentially this substance. If the original condensation is carried out rapidly and no attempt is made to check the development of heat, the product is composed of unsaturated ketone almost free from ketol. This ketone is, however, not identical with that obtained by dehydration of the ketol. It is higher-boiling, denser, and more refractive and readily gives a semicarbazone, m. p. 152°. Both ketones give the analytical figures required for  $\text{C}_7\text{H}_{12}\text{O}$  and the semicarbazones also give the correct analytical values and depress each other's melting point. It is clear that these are two distinct substances, which may represent either structural isomerides differing in the position of the double bond or geometrical isomerides with the same position of the double bond.

Both ketones showed exaltations in the molecular refractivity (1.11 and 1.15 units) and had low iodine addition values (8 and 2%) (Linstead and May, J., 1927, 2565). Again, both resisted the action of ozone but yielded acetic and *n*-butyric acids on complete oxidation with alkaline permanganate. All doubt as to their

constitution was finally removed by the synthesis of the compound with the only possible alternative formula, the  $\beta\gamma$ -isomeride (III), from the acid chloride of  $\Delta^{\beta}$ -*n*-hexenoic acid (Eccott and Linstead, J., 1929, 2153) and zinc methyl iodide. The ketone so prepared,  $\text{CH}_3\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{COMe}$  (III), was a different substance. It had a high iodine addition value (70%), readily yielded propaldehyde on ozonisation, and gave a *semicarbazone*, m. p. 109–110°. No solid compound was formed when it was treated with ethyl sodio-malonate, whereas the other two ketones yielded the same 5-*n*-propyldihydroresorcinol,  $\text{CHPr}\cdot\begin{array}{c} \text{CH}_2-\text{CO} \\ \text{CH}_2-\text{C}(\text{OH}) \end{array}\cdot\text{CH}$  (IV), by this reaction and subsequent hydrolysis. The first two ketones must therefore be regarded as *cis*- and *trans*-modifications of *n*-butylideneacetone about the  $\alpha\beta$ -double bond.

Geometrical isomerism of this type in ketones has only recently been observed and has received no systematic study. Locquin and Heilmann (*Compt. rend.*, 1928, **186**, 705) have isolated two forms of two  $\alpha$ -alkyl unsaturated ketones, and the presence of a similar isomerism in the homomesitones is suggested by certain properties of these substances (Abbott, Kon, and Satchell, J., 1928, 2514). In addition, a number of styryl ketones containing the skeleton  $\text{CHPh}\cdot\text{CH}\cdot\text{COR}$  have been found to exist in coloured and colourless modifications (Haber, *Ber.*, 1891, **24**, 618; McGookin and Heilbron, J., 1924, **125**, 2099, and subsequent papers; Dilthey and Radmacher, *Ber.*, 1925, **58**, 361, *et cet.*). The isomerism shown by these compounds differs materially from that of the butylideneacetones. The isomeric styryl ketones have the same melting points and give identical derivatives (Wilson, Heilbron, and Sutherland, J., 1914, **105**, 2892). They are also noteworthy for the ease with which the less stable pass into the more stable forms.

In determining the configuration of the *n*-butylideneacetones, advantage was taken of their close relationship with  $\Delta^{\alpha}$ -*n*-hexenoic acid. Von Auwers and Wissebach have shown (*Ber.*, 1923, **56**, 715) that solid crotonic acid is almost unquestionably the *trans*-isomeride and von Auwers (*Annalen*, 1923, **431**, 46) found that it is this form of the acid which is produced from acetaldehyde by the Döbner reaction. It is reasonable to suppose that  $\Delta^{\alpha}$ -*n*-hexenoic acid (m. p. 33°), which is the almost exclusive product from *n*-butaldehyde in the Döbner reaction, also has the *trans*-configuration. When its acid chloride was condensed with zinc methyl iodide, the lower-boiling butylideneacetone was obtained, yielding the *semicarbazone* of m. p. 124° in a state of purity. The connexion indicated by this reaction was confirmed by the oxidation of this modification of the ketone with sodium hypochlorite, pure solid  $\Delta^{\alpha}$ -*n*-hexenoic acid

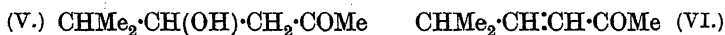
being obtained. As a first assumption, therefore, this butylideneacetone is the *trans*-isomeride and the *cis*-configuration must be assigned to the ketone with semicarbazone of m. p. 152°, prepared by direct condensation. We endeavoured to confirm this view by studying the relative ease of cyclisation of the two ketones, e.g., with concentrated sulphuric acid, to dihydrotoluenes, but deep-seated changes invariably occurred. When the *cis*-ketone was oxidised with sodium hypochlorite, a liquid acid was obtained giving long needles of m. p. 3°. This acid yielded the dibromide and anilide of solid (*trans*-)*n*-hexenoic acid and is regarded as a mixture of this acid with its as yet unknown *cis*-isomeride. It will be further investigated.

The isomeric *n*-butylideneacetones strongly resist configurational changes: for instance, the ketones regenerated from the semicarbazones by dilute acid re-form these derivatives in a state of purity. Bromine in an inert solvent, which has so marked an effect on configurational changes in acids, is rapidly absorbed with no apparent change in the unattacked ketone. Boiling dilute sulphuric acid has no pronounced effect, although it somewhat diminishes the purity of the ketones as measured by the readiness with which they yield pure semicarbazones. Hydrobromic acid, however, combines additively with both isomerides, giving a bromo-ketone which, when decomposed with aqueous potassium bicarbonate, yields the *trans*-ketone. In this way it is possible to convert the *cis*-form into its isomeride.

It was hoped to study the tautomeric change between the  $\beta\gamma$ - and the two  $\alpha\beta$ -ketones under the conditions previously used for such determinations. Unfortunately, all these ketones were readily converted into high-boiling products by the action of alkaline catalysts such as piperidine, sodium ethoxide and even sodium isopropoxide (Kon and Linstead, J., 1929, 1269). The  $\beta\gamma$ -ketone was, however, converted into the *trans*- $\alpha\beta$ -ketone with boiling 20% sulphuric acid (compare Blaise, *loc. cit.*; Kon and Linstead, J., 1925, 127, 815). Treatment in this way for 9 hours yielded a mixture of ketones with an iodine addition value of 32% (equivalent to about 75% of  $\alpha\beta$ -ketone), giving the *trans*- $\alpha\beta$ -semicarbazone, and further treatment did not appreciably affect this. It is remarkable that it was not found possible to produce the  $\beta\gamma$ -ketone—as shown by an increase in iodine addition—from either form of the  $\alpha\beta$ -ketone under these conditions. In any case, it is clear that the  $\alpha\beta$ -position of the double bond is the more stable as in the corresponding acids (Fittig, *Annalen*, 1894, 283, 47; Goldberg and Linstead, J., 1928, 2343). The  $\beta\gamma$ -ketone could also be converted into the  $\alpha\beta$ - by addition and elimination of hydrogen bromide. Here the product had an

iodine addition value of 32% and yielded the semicarbazone of the *trans*- $\alpha\beta$ -ketone. In view of the proved "abnormal" addition of hydrogen bromide to many  $\beta\gamma$ -unsaturated compounds, for example, to  $\Delta^1$ -cyclohexenylacetic acid (Wallach, *Annalen*, 1907, **353**, 289), the bromine entering the  $\beta$ - and the hydrogen the  $\gamma$ -position, it is unnecessary to assume with Blaise (*loc. cit.*) that the first stage in such a process is an isomeric change to the  $\alpha\beta$ -form, followed by a "normal" addition.

Attention was next directed to the isomeric ketones derived from isobutaldehyde. The condensation of this with acetone has been studied by Barbier and Bouveault (*loc. cit.*), who appear to have isolated only a crude product, and by Francke and Kohn (*loc. cit.*), who isolated both a ketol (V), the dehydration of which was not studied, and an unsaturated ketone (VI), b. p. 157°/750 mm.



Kishner (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 987) records the formation of an isobutylideneacetone (semicarbazone, m. p. 162—163°).

Using the method of Francke and Kohn, we isolated an unsaturated ketone which readily yielded a pure semicarbazone of m. p. 126°. The ketol (V) was prepared by a method similar to that used in the *n*-series and was dehydrated by iodine to yield an unsaturated ketone very similar to the first but giving a semicarbazone, m. p. 160°, which depressed the m. p. of the derivative already prepared. Francke and Kohn oxidised their ketone to  $\Delta^{\alpha}$ -isohexenoic acid, and we have confirmed this relationship by synthesising this form of the ketone (semicarbazone, m. p. 126°) from  $\Delta^{\alpha}$ -isohexenoyl chloride and zinc methyl iodide. As before, therefore, the ketone with the lower-melting semicarbazone is taken to be the *trans*-form. To show conclusively that neither form had the  $\beta\gamma$ -structure (VII), this ketone was independently prepared from pyroterebyl chloride (VIII) and zinc methyl iodide.



It is of interest that, although the action of thionyl chloride on pyroterebic acid fails to yield a pure product owing to the addition of hydrogen chloride to the double bond (Linstead, *J.*, 1929, 2498), the action of phosphorus trichloride in benzene gives the unsaturated acid chloride (VIII) in a state of purity. The new ketone (VII) has a high affinity for iodine, whereas the isobutylideneacetones have practically none, and moreover yields a distinct semicarbazone.

It has been shown that the presence of two  $\gamma$ -methyl groups in a three-carbon system is accompanied by great stability of the

$\beta\gamma$ -double bond; for example, in pyroterebic acid (Goldberg and Linstead, *loc. cit.*) and its ethyl ester (Linstead, *loc. cit.*). It was therefore of great interest to find that the ketones in the *iso*-series differed abruptly from those of the normal series in that the  $\beta\gamma$ -were the more stable forms. The *trans*- $\alpha\beta$ -ketone was converted to the extent of some 80% into its  $\beta\gamma$ -isomeride on being boiled with dilute sulphuric acid, and the same change could be effected by the addition and elimination of hydrogen bromide. In some respects these ketones resemble those investigated by Kon (J., 1926, 1792) with a *cyclohexane* ring in place of the  $\gamma$ -gem-dimethyl group.

Another difference between the two series is that on dehydration the *n*-ketol yields the *trans*-, and the *iso*-ketol the *cis*-, form of the unsaturated ketone. Direct condensation under vigorous conditions proceeds differently in the two cases, for the *n*-aldehyde gives a *cis*-ketone, and the *iso*-aldehyde the *trans*-, but this difference appears to depend largely upon the experimental conditions. For instance, Weizmann and Garrard (*loc. cit.*) obtained a fairly pure *trans*-*n*-butylideneacetone by direct condensation, whereas Kishner's ketone (*loc. cit.*) seems to have been the *cis*-form of isobutylideneacetone. In many condensations in the early stages of the present work mixtures of  $\alpha\beta$ -ketones were obtained and it is probably largely a matter of chance that the methods eventually developed to give individual products yielded a *trans*-form in one series and a *cis*-form in the other. In any case, it must be assumed that, whatever the configuration of the final product, the reaction first proceeds through the ketol, which subsequently loses water under the conditions used in the "direct condensation." This being so, it is a matter of interest that the pure *isolated* ketol is not dehydrated when treated with alkali under these conditions.

The investigation of these and related compounds will be continued.

[*Added to proof.*].—The publication of an abstract (A., 1930, 325) has directed our attention to a paper of Locquin and Heilmann (*Bull. Soc. chim.*, 1929, 45, 1126). These authors obtained an *iso*-butylideneacetone of indefinite b. p. which failed to yield a pure semicarbazone. This they regard as indicating the existence of stereoisomeric forms of the ketone and semicarbazone, a view which is amply confirmed by the isolation in the present work of the two individual ketones and their derivatives. There seems little doubt that the  $\beta\gamma$ -ketone of Locquin and Heilmann is identical with ours, but we consider Kishner's ketone, produced by direct condensation (*loc. cit.*), to be the *cis*- $\alpha\beta$ -form and not the  $\beta\gamma$ - as suggested by Locquin and Heilmann. The semicarbazones provide no useful

evidence, but the physical properties of Kishner's ketone agree with those of our  $\alpha\beta$ -forms rather than with those found for the  $\beta\gamma$ - by Locquin and Heilmann and in the present work. Further, Kishner prepared 3-methyl-5-isopropylpyrazoline in 90% yield from his ketone by a reaction which Locquin and Heilmann themselves use as being selective for  $\alpha\beta$ -ketones (*loc. cit.*, p. 1118).

#### EXPERIMENTAL.

##### *Normal Series.*

*Condensation of n-Butaldehyde with Acetone.*—(a) *Production of the ketol.* Grignard and Dubien's method gave good yields of total condensation product, but this always contained a considerable proportion of dehydrated material. The following process caused less dehydration than any other used. To a mechanically stirred mixture of caustic soda (20 g.) in water (40 c.c.) and acetone (116 g.) kept between 5° and 10°, *n*-butaldehyde (72 g.), diluted with acetone (58 g.), was added during 3 hours. After an hour's stirring, the aqueous layer was separated and extracted with ether, and the extract added to the oil. The combined product was neutralised with dilute acetic acid, washed with sodium bicarbonate solution and a little water, and dried over anhydrous potassium carbonate. The acetone and ether were removed by suction and the residue was distilled under reduced pressure. A little water and then a fraction (b. p. 68—92°/12 mm.; 30 g.) containing some unsaturated material distilled over, followed by the ketol (40 g.), b. p. 95°/12 mm.

Reducing the *amount* of caustic soda lowers the yield and reducing its *concentration* by the addition of water has the same effect and results in the formation of high-boiling material derived from the aldehyde.

Heptan-8-ol- $\beta$ -one (II) (Grignard and Dubien, *loc. cit.*) is a pale yellow liquid with a faint odour,  $d_4^{20}$  0.9296,  $n_D^{20}$  1.4357 (Found: C, 64.8; H, 10.7. Calc.: C, 64.6; H, 10.8%). Treatment of the ketol with 25% aqueous caustic soda (8 vols.) at the b. p. or with shaking in the cold for 3 hours gave only unchanged ketol and high-boiling material.

(b) *Production of cis-n-butylideneacetone* (I). To a mixture of acetone (145 c.c.) and 15% aqueous caustic soda (320 c.c.), *n*-butaldehyde (178 c.c.) was added in a slow stream. The vigorous reaction was at first allowed to proceed under reflux and finished by mechanical shaking for 2—3 days. The aqueous layer was extracted with ether and the extract was added to the organic portion, which was then washed with water and dried with calcium chloride. After removal of the low-boiling material, the residue was fractionated under reduced pressure. The crude ketone had b. p. 70°/12 mm.,

but contained water which could not be removed by ordinary drying agents. An equal volume of dry benzene was added which was then distilled off at ordinary pressure through a column (compare Grignard and Dubien, *loc. cit.*). The dry ketone obtained by fractionation of the residue (50 g.) had b. p.  $67-70^{\circ}/12$  mm.,  $d_4^{25}$  0.8507,  $n_D^{25}$  1.4470,  $[R_L]_D$  35.22. The iodine addition value was 4%. This and all other iodine addition values referred to in this paper were obtained by using 10-minute reactions in chloroform solution (Linstead and May, *loc. cit.*). If the amount of alkali and water used in the condensation was similar to that used in the preparation of the ketol, and the reaction was allowed to proceed vigorously, mixtures of ketol and ketone were obtained.

The *cis*-ketone so prepared was nearly free from its isomeride, as shown by the purity of the semicarbazone, which could only be obtained in quantity when the following precautions were observed. The ketone (20 g.) was added to a cold solution of semicarbazide hydrochloride (20 g.) in the minimum quantity of saturated aqueous sodium acetate. Miscibility was established with alcohol, and a seeding crystal introduced together with enough water to prevent its solution. Precipitation of the semicarbazone was allowed to occur at room temperature, the product being cooled in a freezing mixture before filtration. The material so obtained was micro-crystalline, melting at  $143^{\circ}$ , and at  $152^{\circ}$  after one crystallisation. The m. p. could not be further raised (Found: C, 57.1; H, 9.1.  $C_8H_{15}ON_3$  requires C, 56.8; H, 8.9%). The semicarbazone (22 g., m. p.  $152^{\circ}$ ) was intimately mixed with 25 g. of crystallised oxalic acid and the very volatile ketone was distilled in a current of steam, isolated by means of ether, and dried in the manner already described. Yield, 80%.

*cis*-Butylideneacetone so obtained is a colourless pleasant-smelling liquid, b. p.  $70^{\circ}/15$  mm.,  $d_4^{25}$  0.8555,  $n_D^{25}$  1.4505,  $[R_L]_D$  35.22 (calc., 34.07) (Found: C, 74.7; H, 10.7.  $C_7H_{12}O_2$  requires C, 74.9; H, 10.8%). The pure ketone has an iodine addition value of 2.3% and immediately yields the semicarbazone, m. p.  $152^{\circ}$ , in a state of purity.

*Dehydration of the Ketol.*—(i) *With iodine.* By the method of Grignard and Dubien, 40 g. of the ketol yielded 24 g. of ketone, b. p.  $58-62^{\circ}/16$  mm.,  $d_4^{25}$  0.8493,  $n_D^{25}$  1.4408,  $[R_L]_D$  34.8, iodine addition value 23.4%.

(ii) *With acetic anhydride* (Claisen, *Annalen*, 1899, 306, 326). The ketol (42 g.) was refluxed with acetic anhydride (50 g.) for 3 hours. Direct distillation of the product under reduced pressure yielded no evidence of acetylation, the material boiling between  $50^{\circ}$  and  $71^{\circ}/5$  mm. After the addition of an excess of sodium carbonate



the product was distilled in steam and the ketone was isolated in the usual way and redistilled. The product (28 g.) had b. p.  $60^{\circ}/10$  mm.,  $d_4^{25}$  0.8507,  $n_D^{25}$  1.4449,  $[R_L]_D$  35.06, iodine addition 11.2%.

(iii) *With oxalic acid* (Pauly and von Berg, *Ber.*, 1901, **34**, 2092). 32 G. of the ketol were heated on the water-bath for 2 hours with 46 g. of anhydrous oxalic acid. Hydrated oxalic acid crystallised from the reddish-brown syrupy residue, which was distilled in a current of steam. The ketone, isolated in the usual way (19 g.), had b. p.  $62-64^{\circ}/12$  mm.,  $d_4^{25}$  0.8450,  $n_D^{25}$  1.4432,  $[R_L]_D$  35.18, iodine addition 8.2%.

The products obtained by all these methods yielded a *semicarbazone* which crystallised from dilute alcohol in white silvery plates, m. p.  $128^{\circ}$  (Found: C, 56.9; H, 9.2.  $C_8H_{15}ON_3$  requires C, 56.8; H, 8.9%). The product from the iodine dehydration yields this with comparative difficulty, and the oxalic acid method is the most satisfactory for preparing a homogeneous ketone. The ketone from each method contains water which cannot be removed by ordinary drying agents (compare Grignard and Dubien, *loc. cit.*) (Found: C, 72.9; H, 10.4%). Dried by distillation with benzene in the manner already described, *trans-n*-butylideneacetone was obtained as a colourless liquid with a pleasant odour differing somewhat from that of the *cis*-isomeride. It had b. p.  $62^{\circ}/15$  mm.,  $d_4^{25}$  0.8445,  $n_D^{25}$  1.4430,  $[R_L]_D$  35.18, iodine addition 9.0%. Ultimate analysis is difficult and tends to give low results for this type of ketone, as has been noticed by other workers (Claisen, Francke and Kohn, Weizmann and Garrard, *loc. cit.*) (Found: C, 74.3; H, 10.5. Calc.: C, 74.9; H, 10.8%). Unlike the *cis*-ketone, the *trans*-ketone was regenerated from its semicarbazone with considerable loss. In one experiment 16 g. of semicarbazone gave 2 g. of ketone having b. p.  $62^{\circ}/10$  mm.,  $d_4^{25}$  0.8483,  $n_D^{25}$  1.4423, iodine addition 8.1%; and in another, 12 g. yielded 2 g., b. p.  $64^{\circ}/10$  mm.,  $d_4^{25}$  0.8454,  $n_D^{25}$  1.4424. The ketone prepared by the oxalic acid method and purified by distillation with benzene and under reduced pressure was used as *trans*-ketone in the experiments described later.

*trans-Ketone from  $\Delta^2$ -n-Hexenoyl Chloride.*—36 G. of the acid chloride (Goldberg and Linstead, *loc. cit.*) were added to zinc methyl iodide, prepared in the usual way from 41.6 c.c. of methyl iodide and 43 g. of zinc-copper couple in 21.6 c.c. of ethyl acetate and 50 c.c. of benzene (Blaise and Maire, *Ann. Chim. Phys.*, 1908, **15**, 556). A typical product, isolated in the usual way (*loc. cit.*), had b. p.  $69-71^{\circ}/20$  mm., iodine addition 8% (16 g.). This synthesis was carried out many times in the present work, but the physical constants of the products agreed neither among themselves nor

with those already found for the two isomeric ketones, as may be seen from the following table :

	B. p.	$d_{20}^{20}$ .	$n_D^{20}$ .
<i>trans</i> -Ketone .....	62°/15 mm.	0.8445	1.4430
<i>cis</i> -Ketone .....	70/15	0.8571	1.4513
Ketone from acid chloride .....	69—71/20	0.8672	1.4404
" " " .....	69/15	0.8603	1.4420
" " " .....	63/10	0.8786	1.4387
" " " .....	66/10	0.8723	1.4407
" " " .....	62—63/12	0.8658	1.4414

The high density and low refractivity of the material prepared from the acid chloride point to the presence of traces of ester (such as is often produced in these reactions) which cannot be completely removed by fractionation. This impurity somewhat inhibits the formation of the semicarbazone, which is best prepared by mixing the components in a freezing mixture and keeping the mixture ice-cold until crystallisation is at an end. The derivative then separates almost pure, m. p. 124° alone or when mixed with the *trans*-semicarbazone. A mixture with equal parts of the *cis*-semicarbazone melts at 110°.

*Preparation of  $\Delta^8$ -Hepten- $\beta$ -one (III).*— $\Delta^8$ -Hexenoyl chloride was prepared from  $\Delta^8$ -*n*-hexenoic acid which had been purified by one partial esterification (followed by fractionation) (Eccott and Linstead, *loc. cit.*). The purity of this acid chloride was checked by conversion of a small portion into the *p*-toluidide, m. p. 90° (crude), 95—96° after one crystallisation (mixed m. p. 96°). The acid chloride (25 g.), treated exactly as its  $\alpha\beta$ -isomeride, yielded the ketone (12 g.) as a sweet-smelling liquid, b. p. 61—62°/20 mm.,  $d_{20}^{20}$  0.8618,  $n_D^{20}$  1.4290, iodine addition, 71%. The *semicarbazone* crystallised in small white plates, m. p. 109—110° (Found : C, 57.0; H, 8.7.  $C_8H_{15}ON_3$  requires C, 56.8; H, 8.9%). Satisfactory analytical figures could not be obtained for the ketone itself.

*Oxidation of the Ketones.*—*trans*-Butylideneacetone (5 g.) was mixed with saturated sodium carbonate solution (10 g.-mols. per g.-mol. of ketone), and 3% aqueous potassium permanganate added until no more was reduced. The product, worked up in the usual way, yielded 5 g. of total oxidation product: this had a strong odour of acetic acid, which was separated by distillation and converted into acetanilide (m. p. and mixed m. p. 115°). The higher-boiling material was converted into chloride, and butyryl chloride separated by fractionation and identified by conversion into *n*-butyramide (m. p. and mixed m. p. 115°). The *cis*-ketone was treated in the same way and yielded the same products.

Both *cis*- and *trans*-ketones were recovered unchanged after treatment with ozonised oxygen for 20 hours. The  $\beta\gamma$ -ketone (III), however, readily yielded an ozonide. This was decomposed with

water, and the product, after being made alkaline, distilled. The first fraction contained propaldehyde, which was identified as the *p*-nitrophenylhydrazone, m. p. and mixed m. p. 120°.

The *trans*-ketone (11 g.) was added slowly to excess of an ice-cold, freshly prepared solution of sodium hypochlorite. The mixture was removed from the ice and shaken thoroughly for an hour; the temperature then rose sharply. The cold product was extracted with ether to remove unchanged ketone, treated with an excess of sodium sulphite, acidified, and extracted with ether. The residue from the ether yielded an acid (3 g.), b. p. 116—120°/15 mm., which solidified at room temperature and melted after crystallisation at 33°, alone or when mixed with authentic  $\Delta^{\alpha}$ -*n*-hexenoic acid. The anilide had m. p. and mixed m. p. 109—110°.

The *cis*-ketone (11 g.) was oxidised exactly as above and yielded 3 g. of an acid, b. p. 120—126°/14 mm., m. p. 3°,  $d_4^{25}$  1.00,  $n_D^{25}$  1.4520, iodine addition 0.9% (Linstead and May, *loc. cit.*). A mixture of this acid with a quarter of its weight of the acid of m. p. 33° melted at 6° and the m. p. was further raised by the addition of more 33°-acid. The acid slowly yielded the dibromide of the 33°-acid (m. p. and mixed m. p. 68—70°) and readily gave the anilide through the acid chloride (m. p. and mixed m. p. 109°).

5-*n*-Propyldihydroresorcinol (IV).—(a) From the *trans*-ketone. 4.5 G. of the ketone were added to ethyl sodiomalonate made from 0.92 g. of sodium, 18 c.c. of alcohol, and 6.2 g. of the ester, and the mixture was heated on the water-bath under reflux for 3 hours. The solid sodio-compound of the intermediate ester (6 g.) was collected, washed with a little alcohol, and hydrolysed with crystallised sodium carbonate (10 g.) in water (12 c.c.). The product was worked up in the usual way, and the 5-*n*-propyldihydroresorcinol purified by treatment with sodium bicarbonate. From this it was obtained by acidification and extraction as a viscous oil, which gradually solidified (1 g.). On recrystallisation this melted at 107° (Found: C, 69.8; H, 8.9.  $C_9H_{14}O_2$  requires C, 70.1; H, 9.1%). If the solid sodio-compound was not hydrolysed as such but was acidified and the dihydroresorcinol ester itself was extracted before hydrolysis, the solidification of the final product was much delayed. Hydrolysis with baryta yielded gummy products.

(b) Under similar conditions the *cis*-ketone (5 g.) yielded the same product (1 g.), m. p. and mixed m. p. 107°.

Interconversion of the Isomeric Ketones.—Reference data. Mixtures of the  $\beta\gamma$ - and the *trans*- $\alpha\beta$ -ketone reacted with iodine as follows:

% $\alpha\beta$ -ketone	100	90	80	75	66.6	50	33.0	20	0
% Iodine addition .....	8.1	17.5	28.0	30.4	37.6	48.2	58.0	64.6	71.0

(a) *Sodium ethoxide*. The *trans*- $\alpha\beta$ -ketone (7.4 g.) was treated with 1 equiv. of anhydrous *N*-sodium ethoxide (Kon and Linstead, *loc. cit.*, 1929). The entire product boiled above 170°/20 mm. The  $\beta\gamma$ -ketone was also converted into high-boiling material.

(b) *Sodium isopropoxide* gave the same result.

(c) *Barium hydroxide* (compare Hugh, Kon, and Linstead, J., 1927, 2585). The *trans*- $\alpha\beta$ -ketone (2 g.) was mixed with 10 c.c. of 0.17*N*-barium hydroxide, and miscibility established by addition of alcohol. After 4 hours' boiling, the ketone was isolated unchanged ( $d_4^{20}$  0.8757,  $n_D^{19}$  1.4376, iodine addition 2.5%; semicarbazone, m. p. 124°).

(d) *Piperidine*. A mixture of *trans*- $\alpha\beta$ -ketone (4 g.) and piperidine (6.1 g.) was heated under reflux for 2 days on the water-bath and was finally boiled for 2 hours. Only high-boiling material was recovered. The *cis*- $\alpha\beta$ - and the  $\beta\gamma$ -ketone were similarly affected.

(e) *Dilute sulphuric acid*. The *trans*- $\alpha\beta$ -ketone (3 g.) was refluxed with 9 g. of 20% (by weight) sulphuric acid for 8 hours. The ketonic product (1 g.) had b. p. 70°/15 mm., iodine addition 10%, and gave a semicarbazone, m. p. 100° (crude), which yielded the pure *trans*-derivative on recrystallisation (m. p. and mixed m. p. 124°). Similarly treated, the *cis*- $\alpha\beta$ -ketone (3 g.) gave 1 g. of product, b. p. 70°/15 mm., with unchanged iodine addition. After one crystallisation the semicarbazone gave the almost pure *cis*-derivative (m. p. 148°).

The  $\beta\gamma$ -ketone (3 g.), mixed with 6 g. of 20% sulphuric acid, was heated under reflux for 1 hour. The recovered ketone (1.8 g.) had b. p. 63—68°/18 mm.,  $d_4^{20}$  0.8654,  $n_D^{19}$  1.4332, iodine addition 51%. The semicarbazone was a mixture, m. p. 78°, which could not be separated into its constituents. A similar experiment was carried out for 9 hours. The recovered ketone (1.0 g.) had  $d_4^{20}$  0.8680,  $n_D^{19}$  1.4390, iodine addition 32.4%. The semicarbazone melted (crude) at 95—96° and after recrystallisation gave the white plates of the *trans*- $\alpha\beta$ -semicarbazone, m. p. 122°, mixed m. p. 123—124°. In a further experiment, the  $\beta\gamma$ -ketone (5 g.) was treated as before for 9 hours; the product was then isolated and given a further 9 hours' treatment. The final product (2 g.) had  $d_4^{20}$  0.8539, iodine addition 29.4% (equivalent to 77% of *trans*- $\alpha\beta$ -ketone) and yielded the *trans*- $\alpha\beta$ -semicarbazone.

(f) *Hydrobromic acid* (compare Blaise, *loc. cit.*). The *trans*- $\alpha\beta$ -ketone (5 g.) was added slowly to 12 g. of ice-cold hydrobromic acid, saturated at 0°. The black liquid was kept at 0° for  $\frac{1}{2}$  hour and then poured into water and extracted with ether. The extract was washed with sodium bicarbonate solution and dried over anhydrous sodium sulphate. After removal of the solvent the

residue was distilled; the bromo-ketone (4 g.) then came over at  $70^{\circ}/3$  mm. as a colourless liquid, which quickly darkened in light and had a faint characteristic odour distinct from that of the unsaturated ketone. It was boiled with potassium bicarbonate (5 g.) in water (30 c.c.) for 2 hours. The ketone obtained had b. p.  $70^{\circ}/15$  mm.,  $d_4^{25}$  0.8460, and iodine addition 17.3% (an increase of 8.0%). The semicarbazone melted at  $100^{\circ}$  (crude) and yielded the pure *trans*-derivative after recrystallisation (m. p. and mixed m. p.).

Similarly treated, the *cis*-ketone reacted less completely and the crude bromo-ketone was accordingly mixed with a further 12 g. of hydrobromic acid. The bromo-ketone isolated from the product had b. p.  $80^{\circ}/5$  mm. and gave with bicarbonate a ketone the semicarbazone of which melted (crude) at  $100^{\circ}$  and after recrystallisation at  $124^{\circ}$ . Its identity with the *trans*-derivative was confirmed by a mixed melting-point determination.

The  $\beta\gamma$ -ketone (3.5 g.), treated in the same way with hydrobromic acid (8.4 g.), yielded a bromo-ketone, b. p.  $80^{\circ}/5$  mm. The ketone obtained from this by treatment with bicarbonate had b. p.  $72^{\circ}/15$  mm.,  $d_4^{25}$  0.8835,  $n_D^{20}$  1.4337, iodine addition 32%. The crude semicarbazone melted at  $103^{\circ}$  and furnished the pure *trans*- $\alpha\beta$ -derivative on recrystallisation.

#### iso-Series.

*Condensation of isoButaldehyde with Acetone.*—(a) *Production of ketol.* The isobutaldehyde was partly prepared by Fossek's method (*Monatsh.*, 1881, 2, 614) and partly purchased from Messrs. Poulenc Frères. The aldehyde (50 g.) was added during 5 hours with mechanical stirring to a mixture of acetone (100 g.), aqueous caustic soda (50 c.c. of 12%), and ether (20 g.) maintained at  $10^{\circ}$ . The product was isolated as in the *n*-series and yielded 32 g. of the pure ketol and a considerable quantity of dehydrated material.  $\epsilon$ -Methylhexan-8-ol- $\beta$ -one (V) (Francke and Kohn, *loc. cit.*) was thus obtained as a colourless liquid, b. p.  $92^{\circ}/23$  mm.,  $d_4^{25}$  0.9432,  $n_D^{25}$  1.4357 (Found : C, 64.7; H, 10.5. Calc. : C, 64.6; H, 10.8%).

(b) *Production of *trans*-isobutylideneacetone (VI)* (compare Francke and Kohn, *loc. cit.*). *iso*Butaldehyde (50 g.) was added in a slow stream to a mixture of acetone (52 c.c.) and aqueous caustic soda (120 c.c. of 10%). The mixture was subsequently shaken for 2 days and worked up in the usual way. The ketone obtained (20 g.) had b. p.  $63$ — $65^{\circ}/20$  mm.,  $d_4^{25}$  0.8407,  $n_D^{25}$  1.4395,  $[R_L]_D$  35.06 (calc., 34.07), iodine addition 4.5%. The semicarbazone melted in the crude state at  $120^{\circ}$  and formed white silvery plates, m. p.  $126^{\circ}$ , from dilute alcohol (Found : C, 56.7; H, 9.1.  $C_8H_{15}ON_3$  requires C, 56.8; H, 8.9%).

*Dehydration of the Ketol.*—Anhydrous oxalic acid caused considerable charring and only a few drops of material, b. p. 62°/12 mm., could be obtained. This yielded a mixture of semicarbazones.

Dehydration with iodine in the usual manner gave a 70% yield of *cis*-isobutylideneacetone, b. p. 64°/18 mm.,  $d_4^{20}$  0.8558,  $n_D^{20}$  1.4374,  $[R_L]_D$  34.32 (calc., 34.07), iodine addition 8%. The *semicarbazone* crystallised in small plates, m. p. 160° (Found: C, 57.0; H, 9.2.  $C_8H_{15}ON_3$  requires C, 56.8; H, 8.9%). A mixture of equal parts of this and the *trans*-semicarbazone (m. p. 126°) melted at 110°.

$\Delta^{\alpha}$ -isoHexenoyl chloride (Goldberg and Linstead, *loc. cit.*), treated with zinc methyl iodide in the usual way, yielded *trans*-isobutylideneacetone in 45% yield. This had b. p. 64°/23 mm.,  $d_4^{20}$  0.8549,  $n_D^{20}$  1.4357,  $[R_L]_D$  34.22 (calc., 34.07), iodine addition 1%, and was identified with that prepared by direct condensation by the formation of the semicarbazone, m. p. and mixed m. p. 126°.

$\beta\gamma$ -Ketone.—Pyroterebic acid prepared by equilibration of  $\Delta^{\alpha}$ -isohexenoic acid (Goldberg and Linstead, *loc. cit.*) had b. p. 103°/14 mm.,  $d_4^{25}$  0.9694,  $n_D^{25}$  1.4442. It was dissolved (18 g.) in an equal volume of dry benzene, and phosphorus trichloride (10% excess) was cautiously added. The mixture was heated on the water-bath for  $\frac{3}{4}$  hour and then yielded 15 g. of pyroterebyl chloride (VIII), b. p. 54°/15 mm. The *anilide* prepared from this formed flattened needles, m. p. 98°, from benzene and light petroleum (Found: C, 76.1; H, 7.9.  $C_{12}H_{15}ON$  requires C, 76.2; H, 8.0%). Repeated crystallisation failed to raise the melting point: the derivative, m. p. 106°, of Goldberg and Linstead (*loc. cit.*) probably contained some  $\gamma$ -chloroanilide.

Pyroterebyl chloride so prepared gave with zinc methyl iodide a 35% yield of  $\epsilon$ -methyl- $\Delta^{\delta}$ -hexen- $\beta$ -one (VII), b. p. 72–74°/30 mm., obviously contaminated with non-ketonic by-products. It had  $d_4^{25}$  0.9012,  $n_D^{25}$  1.4317, iodine addition 66%, and yielded a very pure *semicarbazone*, which crystallised from dilute alcohol in white silvery flakes, m. p. 158° (crude) and 159–160° (after recrystallisation) (Found: C, 57.0; H, 9.2.  $C_8H_{15}ON_3$  requires C, 56.8; H, 8.9%). A mixture with the *cis*- $\alpha\beta$ -semicarbazone melted at 154°.

*Conversion of the trans- $\alpha\beta$ - into the  $\beta\gamma$ -form.* (a) *With sulphuric acid.* The procedure used in the *n*-series was followed. Reaction for 16 hours almost completely destroyed the ketone, only 10% being recovered. This yielded the  $\beta\gamma$ -semicarbazone, m. p. and mixed m. p. 159–160°. Reaction for 3 hours left 40% of ketone, b. p. 64°/20 mm., iodine addition 51.3% (an increase of 46.8%), which gave the  $\beta\gamma$ -semicarbazone.

(b) *With hydrobromic acid.* This was carried out as in the *n*-series,

two treatments with the reagent being used. The bromo-ketone decomposed slightly on distillation, but a sample of b. p.  $90^{\circ}/5$  mm. was decomposed with bicarbonate in the usual way and yielded the  $\beta\gamma$ -ketone, identified in the form of its semicarbazone. In another experiment, only one treatment with the reagent was given and the bromo-ketone was treated with bicarbonate without distillation: 40% of ketone was recovered, b. p.  $64^{\circ}/20$  mm., iodine addition 52.4%, which readily yielded the  $\beta\gamma$ -semicarbazone, m. p. and mixed m. p.  $159-160^{\circ}$ .

All the unsaturated ketones described in the present communication deteriorate rapidly on keeping with the formation of high-boiling products (compare Weizmann and Garrard, *loc. cit.*). On one occasion an old sample of *cis*-isobutylideneacetone exploded on attempted distillation, which suggests that some type of oxidation occurs.

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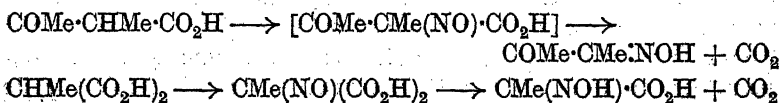
### CXIII.—*The Action of Benzenediazonium Chloride on $\beta$ -Nitroethyl Alcohol and its Derivatives.*

By EDWARD CHARLES SNELL JONES and JAMES KENNER.

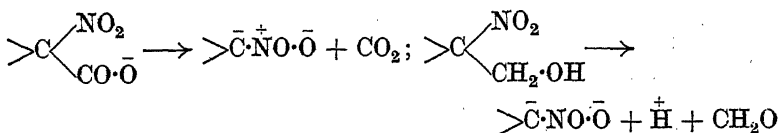
In a previous paper (J., 1928, 2697) it was pointed out that a large proportion of the reactions of nitroso-compounds can be referred to their tendency to pass into oximino-derivatives, and the perception of this, illuminating the nature of Piloty and Ruff's synthesis of glycerol, permitted the generalisation that compounds in which a nitroso- and a methylol group are attached to the same quaternary carbon atom will decompose immediately they are produced, with the formation of an oximino-compound and formaldehyde:



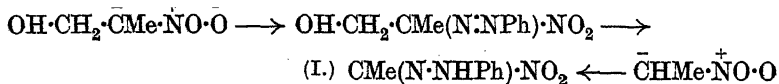
Considering now the methylol rather than the nitroso-group, the reaction in question corresponds to the loss of carbon dioxide undergone when, for example, methylacetoacetic and *isosuccinic* acids are treated with nitrous acid:



Similarly the familiar decomposition of the nitroacetate ion, and its homologues, into the nitro-compound and carbon dioxide corresponds to the elimination of formaldehyde from derivatives of  $\beta$ -nitroethyl alcohol under the influence of sodium methoxide (Schmidt and Wilkendorf, *Ber.*, 1919, 52, 389):

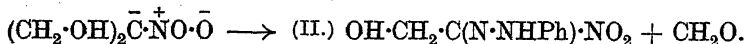


A similar correspondence was observed when the sodium salts of  $\beta$ -nitroethyl alcohol and its derivatives were treated with benzenediazonium chloride in place of nitrous acid. For instance, the  $\omega$ -nitroacetaldehydephenylhydrazone (I) resulting from the interaction of the sodium salt of nitroethane with benzenediazonium chloride was also obtained by the action of the same reagent on the sodium salt of  $\beta$ -nitropropyl alcohol:



The formaldehyde produced was identified as usual in the form of methylenebis- $\beta$ -naphthol.

Similarly,  $\beta$ -nitrotrimethylene glycol was converted into a compound corresponding in composition to  $\omega$ -nitroglycollaldehydephenylhydrazone (II):

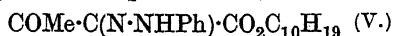
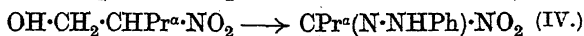
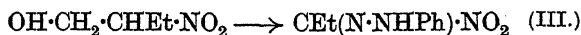


In this instance, however, the product melted at  $117^\circ$ , whereas Demuth and Meyer record a melting point of  $104^\circ$  for the compound obtained from  $\beta$ -nitroethyl alcohol itself (*Annalen*, 1890, 256, 30) and a repetition of their work confirmed their result with the exception that the melting point was raised to  $108^\circ$ . Whereas the specimen of Demuth and Meyer's substance was orange-red and became discoloured after a day or two at the ordinary temperature, (II) was yellow and remained unchanged for a considerable period. Each compound exhibited the normal molecular weight in chloroform solution, and satisfied Bülow's reaction for hydrazones (*Annalen*, 1886, 236, 195). Furthermore, (II) was converted into its isomeride by treatment with aqueous sodium hydroxide or with methylalcoholic sodium methoxide, followed by acidification, whereas the isomeride was recovered unchanged after similar treatment. We therefore regard them as stereoisomerides, assigning the *cis*-configuration to the lower-melting isomeride, and thus relating its



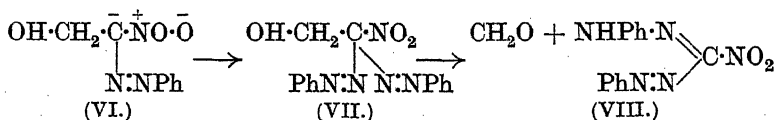
instability to that of the nitrolic acids, which are also regarded as *cis*-compounds (Graul and Hantzsch, *Ber.*, 1898, **31**, 2863).

In no other of the cases investigated and referred to later, did we isolate definite stereoisomerides, although there was some evidence of their formation: for instance, the hydrazones (III) and (IV) were isolated in the first place as red oils, which crystallised only very slowly when inoculated with the pure material (compare also Lapworth, *J.*, 1903, **83**, 1114), but were at once obtained in the solid condition by solution in alkali and precipitation by acid:



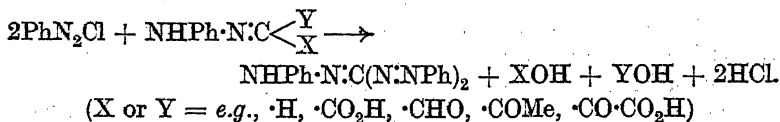
Bamberger and Schmidt have described two forms of nitroformaldehydephenylhydrazone, melting respectively at  $74\cdot5^\circ$  and  $84\cdot5^\circ$  (*Ber.*, 1901, **34**, 2001), but since the two forms are interconvertible by treatment with solvents their relationship would seem to be of a physical rather than a chemical character. Moreover, in a repetition of the preparation of this compound from nitromethane we were able to raise the melting point to  $92^\circ$ .

Although the hydrazone formula for the products of coupling nitro- and other reactive compounds with benzenediazonium chloride has probably been universally accepted since it was put forward by V. Meyer (*Ber.*, 1888, **21**, 11), this would appear to be the first occasion on which the stereoisomerism it involves has received definite experimental verification. The slow mutarotation of menthyl benzeneazoacetoacetate (V) observed by Lapworth (*loc. cit.*) is an indication of isomerism which might, however, be structural rather than spatial. The possibility of structural isomerism in fact is indicated by the behaviour of the above stereoisomeride towards alkali. For the transition of (II) into its isomeride must be regarded as indicating the formation from each of an anion (VI), in which the double bond of the hydrazone group has given place to a single bond. Further evidence on this point is supplied by the behaviour of the hydrazones towards benzenediazonium ions. Thus the formula (VI) shows a negative centre available for coupling:



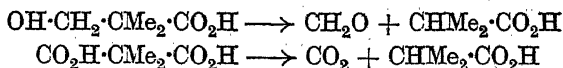
In the light of the foregoing considerations, however, it is clear that the first product (VII) of such a reaction would at once pass into nitroformazyl (VIII) by the loss of formaldehyde. Indeed this series

of changes was observed by Demuth and Meyer (*loc. cit.*) when they studied the interaction of the sodium salt of nitroethyl alcohol with benzenediazonium chloride, and, as we have found, occurs so readily that the nitroacetaldehydephenylhydrazone initially formed can be satisfactorily isolated only when the solution of sodium salt is added to that of the diazonium compound so that no opportunity is afforded for salt formation on the part of the hydrazone. Demuth and Meyer attributed their result to the presence in nitroethyl alcohol (prepared in the usual manner by means of silver nitrite) of a considerable proportion of nitroacetic acid, and suggested that it originated from the action of nitrous acid on the alcohol. This explanation was not challenged either by Bamberger (*Ber.*, 1892, 25, 3201, 3547; 1894, 27, 147, 155), who first assigned the correct constitution to nitroformazyl, or by von Pechmann (*Ber.*, 1892, 25, 3190), who, simultaneously with Bamberger, made an extensive study of the displacement of other groups by the benzeneazo-group, according to the scheme:

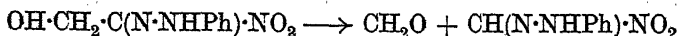


The course of this reaction is presumably analogous to that represented above by the formulæ (VI), (VII), and (VIII).

This property of the methylol group asserts itself in still another direction. For although  $\beta$ -hydroxy-acids in general readily undergo loss of water with formation of  $\alpha\beta$ -unsaturated acids,  $\beta$ -hydroxy- $\alpha\alpha$ -dimethylpropionic acid, lacking an  $\alpha$ -hydrogen atom, undergoes in part a thermal decomposition (Blaise, *Compt. rend.*, 1902, 134, 552; Marcilly, *Bull. Soc. chim.*, 1904, 31, 120) strictly analogous to that of the malonic acids and of various aldols:\*



Similarly, by analogy with the decomposition of nitroacetic acid into nitromethane and carbon dioxide, it might be expected that the thermal decomposition of the hydrazone (II) and its isomeride would, in part, follow the course:

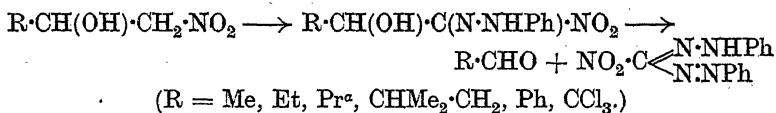


In the case of the *trans*-isomeride, there is no difficulty in observing the production of formaldehyde, but careful regulation of the temperature is requisite in the case of the *cis*-compound to enable the

\* [Added to proof.] The thermal decomposition of ethyl di(hydroxymethyl)-malonate (Welch, *this vol.*, p. 257) is a further example of this reaction.

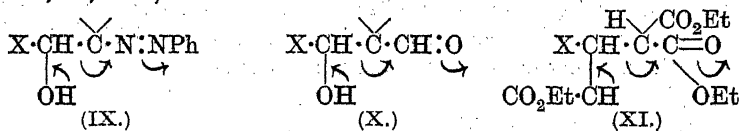
odour of formaldehyde to be detected before the main portion of the material undergoes a complete decomposition, doubtless analogous to that of the nitrolic acids into nitrogen peroxide, nitrogen, and carboxylic acids.

The thermal decomposition of  $\beta$ -hydroxy-acids already mentioned is also exhibited by higher acids, containing alkylol in place of methylol groups (compare, for example, Beilstein's "Handbuch der Organischen Chemie," 4th edition, III, pp. 330—353), and accordingly we have found that quite generally the saturated group  $X\cdot CH\cdot OH$  can be displaced from nitro-compounds in the same manner as the unsaturated groups already enumerated. Thus the reactions represented by the following scheme have been carried out in a number of cases, the ultimate product in each instance being nitroformazyl:



In each case the intermediate hydrazone was isolated and shown to be recovered unchanged from its solution in alkali.

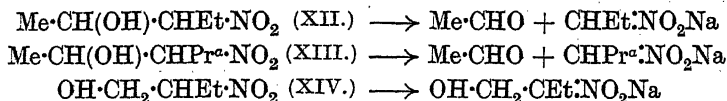
A comparison of (IX), (X), and (XI) shows that the decomposition of the product initially formed from (IX) is formally analogous to the reversals of the aldol condensation (compare, for example, Houben-Weyl, "Methoden der Organischen Chemie," 2nd edition, 1922, 2, 466) and the Michael reaction (compare Knoevenagel, *Annalen*, 1894, 285, 27; Kohler and Conant, *J. Amer. Chem. Soc.*, 1917, 39, 1411):



This comparison assists in substantiating the view that in (X) and (XI), as well as in the thermal decomposition of malonic acids, the initiation of the decomposition is due to an effect transmitted from the carbonyl oxygen atom (compare Cooper, Ingold, and Ingold, *J.*, 1926, 1870), just as in the case of (IX) it is clearly determined by the nitrogen atom attached to the phenyl group. At the same time, however, it must not be overlooked that the cyanohydrins,  $\alpha$ -hydroxy-acids, and, quite generally, compounds of the type  $X\cdot CH(OH)Y$  tend to decompose into  $X\cdot CHO$  and  $HY$ , and that the reversal of the aldol change can be formulated in this manner.

There is also an evident analogy between the aldol condensation and that of aldehydes with nitro-compounds. Correspondingly, we

have found that with increase in complexity of the groups X and Y the stability of the compound  $X\cdot CH(OH)\cdot CHY\cdot NO_2$  towards alkali diminishes, as has been observed in the case of aldols. For instance, whereas the methylol derivatives prepared from nitroethane,  $\alpha$ -nitropropane, and  $\alpha$ -nitrobutane are convertible into their sodium salts, analysis of those prepared from the ethylol derivatives shows that  $\gamma$ -nitropentan- $\beta$ -ol (XII) and  $\gamma$ -nitrohexan- $\beta$ -ol (XIII) suffer decomposition by alkali:



Under the same conditions, however, the desired sodium salt was obtained from  $\beta$ -nitrobutyl alcohol (XIV).

These various salts, on treatment with benzenediazonium chloride, yielded hydrazones in accordance with the principles already discussed.

#### EXPERIMENTAL.

*$\omega$ -Nitroacetaldehydephenylhydrazone from  $\beta$ -Nitropropyl Alcohol.*—A solution of the sodium salt of  $\beta$ -nitropropyl alcohol (J., 1928, 2697) (12.7 g.) in water (125 c.c.) was gradually added to a solution prepared from aniline (9.3 g.), water (125 c.c.), hydrochloric acid ( $d$  1.17; 22 c.c.), and sodium nitrite (6.9 g.). The product (17 g.), isolated by extraction with ether, crystallised from methyl alcohol in yellow plates, m. p.  $149^\circ$  (Found: C, 53.5; H, 5.15. Calc. for  $C_8H_9O_2N_3$ : C, 53.6; H, 5.1%). By the procedure previously described (*loc. cit.*), formaldehyde in the aqueous liquor was identified in the form of methylenebis- $\beta$ -naphthol, m. p.  $205^\circ$ , which did not depress the melting point of an authentic specimen.

The phenylhydrazone was also directly prepared for purposes of comparison by gradual addition of a solution of nitroethane (7.5 g.) and sodium hydroxide (4 g.) in water (100 c.c.) to a diazonium solution prepared as above. The product (16.2 g.) also melted at  $149^\circ$  (Bamberger, *Ber.*, 1898, **31**, 2629, gives  $141$ – $142^\circ$ ) and did not depress the melting point of the above material. Each product was recovered unchanged from its solution in sodium hydroxide.

*$\omega$ -Nitroglycollaldehydephenylhydrazones.*—(1) When a solution of the sodium salt of  $\beta$ -nitrotrimethylene glycol (8.3 g.) in water (50 c.c.) was gradually added to a solution (50 c.c.) prepared from aniline (3.73 g.), hydrochloric acid ( $d$  1.17; 8 c.c.), and sodium nitrite (2.76 g.), a crystalline separation (7.6 g.) was soon produced. On recrystallisation from acetone, stout yellow prisms (II), m. p.  $117$ – $118^\circ$ , were obtained (Found: C, 49.0; H, 4.9; N, 21.6;

*M*, 187.  $C_8H_9O_3N_3$  requires C, 49.2; H, 4.65; N, 21.6%; *M*, 195). Methylenebis- $\beta$ -naphthol, prepared from the aqueous liquor as in the previous case, melted at 205—206°, as also did a sample prepared from the solution obtained by carefully heating the hydrazone in a water-bath at 85° under reduced pressure and absorbing the gases evolved in water. At 110°, oxides of nitrogen accompanied the formaldehyde. This decomposition of the hydrazone also asserted itself when its methyl-alcoholic solution was concentrated.

(2) A solution of the sodium salt of  $\beta$ -nitroethyl alcohol (3.9 g.) (compare *J.*, 1928, 269) was gradually added to a diazonium solution (70 c.c.) prepared from aniline (3.2 g.), hydrochloric acid (*d* 1.17; 7 c.c.), water and sodium nitrite (2.4 g.). The product (6.3 g.) melted at 108—109° after crystallisation from methyl alcohol (Found: C, 49.4; H, 4.7; N, 21.6%; *M*, 201, 189). Formaldehyde could not be detected as a product of treatment of the hydrazone with warm methyl-alcoholic sodium methoxide or aqueous sodium hydroxide, and the material was recovered unchanged. The same compound was obtained by acidifying a solution of the isomeride, m. p. 117—118°, in aqueous sodium hydroxide or in sodium methoxide. A mixture of the isomerides melted at 100—102°. When the hydrazone was very cautiously heated, the odour of formaldehyde was distinctly perceptible, but further decomposition supervened so closely that it was not possible to collect and identify the aldehyde as was done in the previous instance.

By treating the hydrazone (1.95 g.) with a solution of sodium hydroxide (0.4 g.) in water (20 c.c.) and mixing the whole with a diazonium solution (40 c.c.) prepared from aniline (0.93 g.), nitroformazyl (2.1 g.), m. p. 162—163°, was obtained; this did not depress the melting point of an authentic specimen prepared from nitromethane. The odour of formaldehyde was very noticeable in the concentrated ethereal extract, and it was identified as in previous cases. A similar experiment was performed with (II), and nitroformazyl was also produced when a diazonium solution was gradually added to an aqueous solution of the sodium salt of  $\beta$ -nitrotrimethylene glycol.

*Nitroformaldehydephenylhydrazone*.—When a diazonium solution from aniline (9.3 g.), hydrochloric acid (*d* 1.17; 24.4 c.c.), water (125 c.c.), and sodium nitrite (6.9 g.) was gradually added to a solution of nitromethane (6.1 g.) and sodium hydroxide (4 g.) in water (100 c.c.), a mixture of the desired hydrazone with nitroformazyl was produced. The latter was removed by repeated crystallisation from methyl alcohol and the hydrazone was ultimately obtained in orange prisms, m. p. 92° (Found: C, 50.7; H, 4.5; N, 25.7. Calc. for  $C_7H_8O_2N_3$ : C, 50.9; H, 4.3; N, 25.4%).

*Other Examples of the Elimination of Formaldehyde from Nitromethylol Derivatives.*— $\beta$ -Nitrobutyl alcohol, b. p. 122—125°/24 mm. (Pauwels, *Bull. Acad. Sci. Belg.*, 1897, **34**, 651), was converted into its sodium salt (Na, 15.8%), which was coupled with benzenediazonium chloride in the manner described for the case of  $\beta$ -nitropropyl alcohol. The oily phenylhydrazone had only partly crystallised after 4 days, but by precipitation of its solution in aqueous sodium hydroxide the solid hydrazone was at once obtained; it melted at 103—104° after crystallisation from methyl alcohol and did not depress the melting point of the product prepared from nitropropane in brilliant red needles, m. p. 103—104° (N, 21.9%). In the latter case no difficulty was experienced in regard to the solidification of the hydrazone. Bamberger (*Ber.*, 1898, **31**, 2631) gives m. p. 98—99°.

$\beta$ -Nitroamyl alcohol, prepared by adding a few grains of potassium carbonate to a mixture of nitrobutane (12 g.) and formaldehyde (40% solution; 8.75 c.c.) and leaving the mixture for 12 hours after the initial reaction was over, boiled at 130—136°/28 mm. (Found: N, 10.4.  $C_5H_{11}O_3N$  requires N, 10.5%). From its sodium salt (Found: Na, 15.1.  $C_5H_{10}O_3NNa$  requires Na, 14.8%), an oily phenylhydrazone was obtained which did not crystallise when inoculated with the solid material. This was, however, readily obtained by acidifying the solution of the oil in aqueous alkali, and separated from methyl alcohol in brilliant red needles, m. p. 63—66° (Found: N, 20.6.  $C_{10}H_{13}O_2N_3$  requires N, 20.3%). The same compound was obtained directly from the sodium salt of nitrobutane, the crude hydrazone solidifying as in the case of that prepared from nitropropane.

$\beta$ -Nitro- $\beta$ -hydroxymethylamyl alcohol, also formed in small amount in the preparation of the nitroamyl alcohol just described, was isolated as the non-volatile residue from the distillation of the nitroamyl alcohol. After crystallisation from alcohol it melted at 80—83° (Found: N, 8.9.  $C_6H_{13}O_4N$  requires N, 8.6%), and its constitution was established by treatment with sodium ethoxide, the sodium salt of the nitroamyl alcohol (Na, 15.0%), itself identified by conversion into the phenylhydrazone, m. p. 63—66°, just described, being produced.

*Displacement of Other Aldehydes as a Consequence of Coupling.*—The sodium salt of nitroisopropyl alcohol (Henry, *Bull. Acad. Roy. Belg.*, 1895, **15**, 999), on treatment with benzenediazonium chloride, was converted into a phenylhydrazone,  $CHMe(OH) \cdot C(NO_2) \cdot N \cdot NHPh$ , which formed felted orange needles, m. p. 126—127° (Found: C, 51.65; H, 5.5.  $C_9H_{11}O_3N$  requires C, 51.65; H, 5.3%). From  $\alpha$ -nitrobutan- $\beta$ -ol (Henry, *ibid.*, 1896, **15**, 1223) in the same

way, a *sodium* salt (Found: Na, 16.3.  $C_4H_8O_3NNa$  requires Na, 16.3%) and a *phenylhydrazone*,  $CH_3Et(OH) \cdot C(NO_2) : N \cdot NPh$ , bright red needles, m. p. 100—102° (Found: N, 18.9.  $C_{10}H_{13}O_3N_3$  requires N, 18.9%), were successively obtained.

$\alpha$ -Nitropentan- $\beta$ -ol was prepared by condensation of nitromethane (33 g.) with *n*-butaldehyde (39 g.) in presence of water (10 c.c.) and potassium carbonate (0.2 g.). Since no particular rise in temperature was observed, the mixture was heated for some time at 60°, until the aqueous layer (originally the lower) was displaced by the specifically heavier condensation product. After 12 hours, the mixture was worked up and the alcohol (44 g.) isolated as a viscous oil, b. p. 117°/17 mm. (Found: N, 10.8.  $C_5H_{11}O_3N$  requires N, 10.5%). From the *sodium* salt (Found: Na, 14.6.  $C_5H_{10}O_3NNa$  requires Na, 14.8%),  $\alpha$ -chloro- $\alpha$ -nitropentan- $\beta$ -ol was prepared by direct chlorination; it separated from a mixture of equal volumes of chloroform and ethyl acetate in fine needles, m. p. 38° (Found: N, 8.6.  $C_5H_{10}O_3NCl$  requires N, 8.4%). The *phenylhydrazone* obtained from the sodium salt crystallised from methyl alcohol in brilliant red needles, m. p. 92—94° (Found: N, 18.1.  $C_{11}H_{15}O_3N_3$  requires N, 17.7%).

$\alpha$ -Nitrohexan- $\beta$ -ol (Mousset, *Bull. Acad. Roy. Belg.*, 1901, 26, 622) yielded a *sodium* salt (Found: Na, 13.3.  $C_6H_{12}O_3NNa$  requires Na, 13.6%), and a *phenylhydrazone*, which separated from methyl alcohol in bright red needles, m. p. 108—111° (Found: N, 16.7.  $C_{12}H_{17}O_3N_3$  requires N, 16.7%). The chloro-derivative, analogous to that described above, was obtained as an oil which could not be induced to crystallise.

$\gamma\gamma\gamma$ -Trichloro- $\alpha$ -nitropropan- $\beta$ -ol, m. p. 48—49° (Henry, *Bull. Acad. Roy. Belg.*, 1896, 15, 1223, gives m. p. 42—43°), was for obvious reasons not converted into its sodium salt, but coupled in dilute aqueous solution immediately after addition of sodium hydroxide (1 mol.). The resulting *phenylhydrazone* crystallised from methyl alcohol in red prisms, m. p. 129° (Found: N, 13.6.  $C_9H_8O_3N_3Cl_3$  requires N, 13.5%).

The sodium salt of  $\beta$ -nitro- $\alpha$ -phenylethyl alcohol (Rosenmund, *Ber.*, 1913, 46, 1037) yielded a *phenylhydrazone*, which crystallised from methyl alcohol in fine red needles, m. p. 126° (Found: N, 15.8.  $C_{14}H_{13}O_3N_3$  requires N, 15.5%).

The following details are typical of the procedure followed in converting each of the above-mentioned phenylhydrazones into nitroformazyl: a diazonium solution (100 c.c.) prepared from aniline (0.93 g.), hydrochloric acid (*d* 1.12; 2.2 c.c.), water, and sodium nitrite (0.69 g.) was added to a cold solution of the phenylhydrazone from methylnitropentanol (2.5 g.) and sodium hydroxide (0.4 g.)

in water (100 c.c.), and the precipitate purified by crystallisation from methyl alcohol.

$\gamma$ -Nitrobutan- $\beta$ -ol (Henry, *Bull. Acad. Roy. Belg.*, 1896, **15**, 1224) yielded a *sodium* salt which was purified by addition of ether to its solution in methyl alcohol (Found: Na, 16.7.  $C_4H_8O_3NNa$  requires Na, 16.3%), from which a phenylhydrazone, m. p. 148—149°, was prepared (Found: N, 23.5%). The liquor from the coupling process exhibited reducing properties and responded to Simon's test for acetaldehyde, and the phenylhydrazone did not depress the melting point of the phenylhydrazone prepared from nitroethane.

*Decomposition of Derivatives of Nitroisopropyl Alcohol by Alkali.*—When a solution of  $\gamma$ -nitropentan- $\beta$ -ol (Henry, *Bull. Acad. Roy. Belg.*, 1896, **15**, 1223) (Found: N, 10.3%) (13.5 g.) in alcohol (25 c.c.) was treated with a solution of sodium (2.3 g.) in alcohol (42 c.c.), a *sodium* salt was precipitated (Found: Na, 19.9%), and the presence of acetaldehyde in the liquor was demonstrated by Simon's test. The salt was purified by addition of ether to its solution in methyl alcohol (Found: Na, 20.7.  $C_5H_{10}O_3NNa$  requires Na, 20.7%).

$\gamma$ -Nitrohexan- $\beta$ -ol (36.5 g.), b. p. 122.5°/17 mm. (Found: N, 10.0, 10.2.  $C_6H_{12}O_3N$  requires N, 9.5%), was prepared by addition of two drops of aqueous potassium hydroxide solution (50%) to a mixture of nitrobutane (50 g.), acetaldehyde (22 g.), and water (10 c.c.). A *sodium* salt was prepared in the same manner as in the previous instance (Found: Na, 18.2.  $C_4H_8O_3NNa$  requires Na, 18.4%), and the presence of acetaldehyde in the mother-liquor was again indicated by Simon's test.

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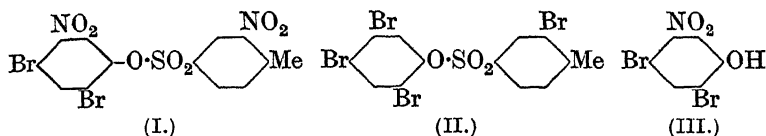
#### CXIV.—*The Scission of Diaryl Ethers and Related Compounds by Means of Piperidine. Part III. The Nitration of 2:4-Dibromo-2':4'-dinitrodi-phenyl Ether and of 2:4-Dibromophenyl p-Toluenesulphonate and Benzoate. The Chlorination and Bromination of m-Nitrophenol.*

By ROSALIND VENETIA HENLEY and EUSTACE EBENEZER  
TURNER.

IN continuation of previous work (Part II, J., 1929, 512), the nitration of 2:4-dibromophenyl p-toluenesulphonate has been investigated. The sole product of dinitration was 2:4-dibromo-



5-nitrophenyl *o*-nitro-*p*-toluenesulphonate (I), the constitution of which was established by its conversion successively into 2:4-di-



bromo-5-aminophenyl *o*-amino-*p*-toluenesulphonate and 2:4:5-tribromophenyl *o*-bromo-*p*-toluenesulphonate (II). The latter substance was converted by piperidine at 100° into 2:4:5-tribromophenol, identical with the product obtained by the replacement of the amino-group by hydroxyl in 2:4:5-tribromoaniline.

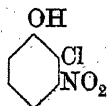
When 2:4-dibromo-5-nitrophenyl *o*-nitro-*p*-toluenesulphonate was heated with piperidine, there were formed 1-*o*-nitro-*p*-toluenesulphonylpiperidine and 2:4-dibromo-5-nitrophenol (III), the constitution of which is determined by that of the above tribromophenol. After crystallisation from light petroleum, with subsequent normal drying, the dibromonitrophenol melted at 77–78°, and an identical product was obtained by nitrating 2:4-dibromophenyl benzoate, followed by hydrolysis. It seemed probable that the compound obtained by Garzino (*Atti R. Accad. Sci. Torino*, 1889, 25, 250) by nitrating 2:4-dibromophenyl propionate should also be 2:4-dibromo-5-nitrophenol, but he gave the m. p. as 90–91°. Crystallisation of our compound from dilute acetone gave a *monohydrate*, m. p. 92–94°, which is probably the product obtained by Garzino.

Another dibromonitrophenol, m. p. 91°, was described by Lindner (*Ber.*, 1885, 18, 612) as resulting from the dibromination of *m*-nitrophenol, and in Beilstein's "Handbuch" (4th Edn., Vol. VI, 246, 248) it is suggested that this compound is possibly identical with Garzino's dibromonitrophenol. In view of the fact (Part II) that *m*-nitrophenol is dichlorinated in the 2- and 4-positions, it at first seemed unlikely that the dibromination would proceed so differently, and we have accordingly investigated the bromination of *m*-nitrophenol afresh.

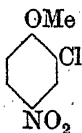
Attempts to prepare the dibromo-compound according to Lindner's directions did not yield any chemically pure substance. When, however, bromine, diluted with carbon dioxide, was passed through *m*-nitrophenol at 120–140°, until the latter acquired the correct increase in weight, and the product was worked up exactly in accordance with Lindner's instructions, material was obtained which behaved as regards crystallisation as an individual, melted at 82–98°, and appeared to be a mixture of 4-bromo- and 2:4:6-tribromo-3-nitrophenol.

When an attempt was made to dibrominate *m*-nitrophenol in glacial acetic acid in presence of anhydrous sodium acetate, the tribromo-compound, m. p. 89—90°, was alone isolated. This substance, m. p. 85°, was obtained by Lindner (*loc. cit.*) by brominating *m*-nitrophenol, and by Daccomo (*Ber.*, 1885, **18**, 1167) by nitrating 2:4:6-tribromophenyl benzoate. Its constitution has now been definitely proved by converting it in stages into 2:3:4:6-tetrabromophenol. Monobromination of 4-bromo-3-nitrophenol also failed to give a dibromo-3-nitrophenol.

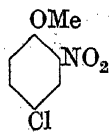
In preparing the monobromo-derivatives of *m*-nitrophenol, we again encountered conflicting results. Pfaff (*Ber.*, 1883, **17**, 612) treated *m*-nitrophenol with bromine in the cold, and described his monobromo-compound as bright yellow needles melting at 110°. Lindner (*loc. cit.*) and Schlieper (*Ber.*, 1892, **25**, 552), using similar methods, obtained what they took to be Pfaff's substance, but they gave the m. p. as 147—148°. Schlieper (*Ber.*, 1893, **26**, 2469) regarded this substance as 2-bromo-3-nitrophenol, since he had obtained the following evidence that the analogous chloro-compound was 2-chloro-3-nitrophenol (IV): the chloro-compound was methylated, and the ether reduced and then deaminated. The product obtained was thought by Schlieper to be *o*-chloroanisole for two reasons: (1) it had the correct b. p., and (2) nitration gave a chloro-nitroanisole, m. p. 93—94°, which he took to be (V), because a substance having this constitution and this m. p. had been described by Fischli (*Ber.*, 1878, **11**, 1463). It seemed possible, however, that Schlieper's chloronitrophenol was the 4-compound, in which



(IV.)



(V.)



(VI.)

case his chloronitroanisole would be (VI), which melts at 97.5° (Reverdin, *Ber.*, 1893, **26**, 1689).

We have found that the monobromination of *m*-nitrophenol at 120—140° (the lowest temperature at which bromination is practicable) gives a mixture of products, at least 50% of which is 4-bromo-3-nitrophenol, m. p. 146.5—147.5°, the constitution of which has been established by its synthesis from *ON*-diacetyl-3-nitro-*p*-aminophenol. Schlieper's supposed 2-bromo-compound is therefore 4-bromo-3-nitrophenol, which substance has indeed already been prepared (Heller and Kammann, *Ber.*, 1909, **42**, 2179) from 3-nitro-*p*-aminophenol.

Monobromination of *m*-nitrophenol in glacial acetic acid in

presence of sodium acetate gave indefinite results, but in absence of sodium acetate the product was a monobromo-compound, m. p. 118.5—121°. This we at first thought to be 2-bromo-3-nitrophenol, and in order to prove its constitution, we converted it into the *p*-toluenesulphonyl derivative, reduced the latter, and replaced the amino-group by bromine. During the last stage, the *p*-toluenesulphonyl group was removed by hydrolysis and a dibromophenol, m. p. 73—74°, was formed. At the same time we performed an analogous synthesis, starting from 3-bromo-2-nitrophenol. The dibromophenol obtained in the second synthesis melted at 68—69°, was different from the first, and was clearly the hitherto unknown 2:3-dibromophenol. It therefore seemed certain that the isomeric compound was 2:5-dibromophenol. Raiford and Bren (*J. Amer. Chem. Soc.*, 1929, 51, 2539) recently attempted the preparation of this substance from 2:5-dibromoaniline. It has now been obtained in excellent yield by applying the method of Noetting and Kopp (*Ber.*, 1905, 38, 3506) to this base, and was found to be identical with the product from the bromo-3-nitrophenol, which is therefore the 6-derivative (2-bromo-5-nitrophenol) already described by Heller and Kammann (*loc. cit.*), who obtained it from 5-nitro-2-aminophenol.

Although it has already been shown (Part II) that *m*-nitrophenol is readily converted into 2:4-dichloro-3-nitrophenol, the above results made it desirable to investigate the monochlorination. Schlieper (*Ber.*, 1893, 26, 2466), by direct chlorination of *m*-nitrophenol, obtained a compound, m. p. 120°, which, as is shown above, may be either the 2- or the 4-chloro-compound. Meldola and Eyre (*J.*, 1902, 81, 996) agreed with Schlieper's conclusion that this was the 2-chloro-compound; they obtained 4-chloro-3-nitrophenol, m. p. 126—127°, by synthesis from 3-nitro-*p*-aminophenol.

We find that monochlorination of *m*-nitrophenol at 120—140° gives approximately equal amounts of 4-chloro-3-nitrophenol (A), m. p. 127—128°, and 2-chloro-3-nitrophenol (B), m. p. 120°. A was identical with a specimen prepared from *ON*-diacetyl-3-nitro-*p*-aminophenol, and the constitution of B follows from two facts: (1) dichlorination of *m*-nitrophenol under similar conditions gives the 2:4-dichloro-compound in good yield, and (2) reduction of B, followed by replacement of the amino-group by chlorine, gives 2:3-dichlorophenol. Although the first of these appears to be sufficient proof, it was desired to prove beyond doubt that B was not 6-chloro-3-nitrophenol (m. p. 118—119°; prepared synthetically by Meldola, Woolcott, and Wray, *J.*, 1896, 69, 1322).

It is therefore possible that, in this case, Schlieper actually had a 2-chloro-compound, but it is difficult to believe this, since the

4-chloro-compound, which was presumably present, is so readily isolated.

We have not investigated the iodination of *m*-nitrophenol, as the statements in the literature seem to be accurate. Schlieper (1893, *loc. cit.*) described the monoiodo-compound as the 2-iodo-derivative, m. p. 134°, and Datta and Prosad (*J. Amer. Chem. Soc.*, 1917, 39, 441) state that iodination in the 2-position proceeds quantitatively. There seems little doubt that this substance is different from the 4- and the 6-iodo-derivative, m. p. 156° and 146–147° respectively (Hähle, *J. pr. Chem.*, 1891, 43, 72; Meldola and Eyre, P., 1901, 238).

In endeavouring to prepare 4-bromo-3-nitrophenol by a different method, we nitrated *N*-*p*-bromophenylphthalimide in presence of excess of concentrated sulphuric acid, expecting to obtain a considerable proportion of the *m*-nitro-derivative (compare Brady, Quick, and Welling, J., 1925, 127, 2264). The main product, however, was the *o*-nitro-derivative. This result is interesting, since nitration of *p*-bromoaniline in presence of excess of sulphuric acid gives almost entirely the *m*-nitro-compound (Noelting and Collin, *Ber.*, 1884, 17, 261) (see Experimental).

The nitration of 2:4-dibromo-2':4'-dinitrodiphenyl ether proceeds similarly to that of the analogous dichloro-compound and gives 2:4-dibromo-5:2':4'-trinitrodiphenyl ether. This ether readily undergoes scission by piperidine into 2:4-dibromo-5-nitrophenol and *N*-2':4'-dinitrophenylpiperidine.

#### EXPERIMENTAL.

2:4-Dibromophenyl *p*-toluenesulphonate, readily obtained by the usual type of process, crystallised from glacial acetic acid in colourless plates, m. p. 120° (Found: Br, 39.8.  $C_{13}H_{10}O_3Br_2S$  requires Br, 39.4%).

*Dinitration of 2:4-Dibromophenyl p-Toluenesulphonate.*—The compound was added to 10 parts of nitric acid (*d* 1.5), the resulting solution being left for an hour and then poured into a large bulk of water. Filtration, followed by crystallisation from glacial acetic acid, gave 2:4-dibromo-5-nitrophenyl *o*-nitro-*p*-toluenesulphonate in pale greenish-yellow leaflets, m. p. 122–123° (Found: Br, 32.6.  $C_{13}H_8O_7N_2Br_2S$  requires Br, 32.3%).

2:4-Dibromo-5-nitrophenol.—The last-mentioned compound was heated for 1 hour at 100° with 2 parts of piperidine. No piperidine hydrobromide separated. Excess of dilute alkali was added, and the solution shaken with benzene; this extracted the 1-*o*-nitro-*p*-toluenesulphonylpiperidine, but, contrary to expectation, it also extracted the piperidine salt of the phenol. It was therefore shaken

with dilute hydrochloric acid and then with alkali. Acidification of the alkaline solution precipitated 2:4-dibromo-5-nitrophenol. This crystallised from light petroleum (b. p. 80—100°) in long yellow needles, m. p. (after being dried over-night in a vacuum over concentrated sulphuric acid) 77—78° (Found: Br, 53.5.  $C_6H_3O_3NBr_2$  requires Br, 53.9%), and from very dilute acetone as the hydrate,  $C_6H_3O_3NBr_2 \cdot H_2O$ , in long yellow needles, m. p. 92—94° (with previous softening), the m. p. depending on the rate of heating (0.5236 g. lost 0.0309 g. in 14 days in a vacuum over phosphoric oxide. Loss of  $1H_2O$  requires 0.0299 g. The specially dry material so obtained melted at 84—86°).

2:4-Dibromo-5-aminophenyl *o*-Amino-*p*-toluenesulphonate.—The corresponding dinitro-compound was added with shaking to a hot solution of stannous chloride (1.5 times the calculated quantity) in a mixture of glacial acetic acid and concentrated hydrochloric acid. After the mixture had been heated at 100° for a few minutes, vigorous reduction set in, and was allowed to become complete during an hour at 100°. The resulting solution was poured into excess of 20% potassium hydroxide solution, and the suspension was cooled and filtered (asbestos). The washed and dried precipitate crystallised from dilute acetone in colourless leaflets, m. p. 174—175° (Found: Br, 37.5.  $C_{13}H_{12}O_3N_2Br_2S$  requires Br, 36.7%).

2:4:5-Tribromophenyl *o*-Bromo-*p*-toluenesulphonate.—The di-amino-compound was diazotised at 20—25°, in a mixture of equal parts of concentrated hydrochloric acid and water, with a solution of sodium nitrite. The diazo-perbromide was precipitated by means of a solution of bromine in aqueous potassium bromide, collected, washed, and decomposed in glacial acetic acid, the temperature of the latter being slowly raised until the b. p. was reached. Water was added, and the precipitate crystallised from alcohol, colourless leaflets, m. p. 107—108°, being obtained (Found: Br, 56.9.  $C_{13}H_8O_3Br_4S$  requires Br, 56.7%).

2:4:5-Tribromophenol.—(a) A solution of the preceding compound in excess of piperidine was boiled under reflux for an hour; the solution was then strongly acidified and submitted to steam distillation. The tribromophenol passed over rapidly, and crystallised from light petroleum (b. p. 40—60°) in long colourless needles, m. p. 85—86° (Found: Br, 73.0.  $C_6H_3OBr_3$  requires Br, 72.5%).

(b) 2:4:5-Tribromoaniline, prepared for the purpose from *p*-dibromobenzene, was converted into the corresponding phenol by adapting the method of Noelting and Kopp (*loc. cit.*). The product was identical with that from process (a).

Kohn and Pfeifer (*Monatsh.*, 1927, 48, 211) obtained what was

evidently mainly 2:4:5-tribromophenol, m. p. 79°, by heating pentabromophenol with zinc dust and glacial acetic acid. We failed to trace this work for some time, since in the original paper and in the British abstracts the substance was incorrectly called 3:4:6-tribromophenol.

*Nitration of 2:4-Dibromo-2':4'-dinitrodiphenyl Ether.*—The ether, described by Le Fèvre, Saunders, and Turner (J., 1927, 1168), is more conveniently obtained as follows: 21 g. of 2:4-dibromophenol were added to 4.6 g. of potassium hydroxide previously fused with 0.5 c.c. of water. To the still hot mixture were added 17.5 g. of 1-chloro-2:4-dinitrobenzene. After a few minutes' shaking, potassium chloride began to separate, and after an hour's heating at 100°, interaction was complete. Excess of dilute alkali was added, and the mixture cooled and shaken. The solid mealy product was collected, washed with water, and crystallised from glacial acetic acid (23 g., m. p. 133°).

The ether was added rapidly to 10 parts of nitric acid (*d* 1.5). After 0.5 hour, the solution was poured into water. The precipitated solid was collected, washed, and crystallised from glacial acetic acid, 2:4-dibromo-5:2':4'-trinitrodiphenyl ether being obtained in very pale yellow needles, m. p. 142° (Found: Br, 35.1.  $C_{12}H_5O_7N_3Br_2$  requires Br, 34.9%).

*Scission of 2:4-Dibromo-5:2':4'-trinitrodiphenyl Ether.*—(a) *With piperidine.* The trinitro-compound was heated with twice its weight of piperidine at 100° for an hour. The solution was treated with alkali and extracted several times with benzene. The benzene layer was extracted first with hydrochloric acid and then with alkali. Acidification of the alkaline solution gave 2:4-dibromo-5-nitrophenol, identical with the above product, and the benzene layer yielded 2:4-dinitrophenylpiperidine.

(b) *With aniline.* The trinitro-compound was heated for an hour at 100° with excess of aniline. On addition of much dilute hydrochloric acid, 2:4-dinitrodiphenylamine separated in almost quantitative yield.

*Nitration of 2:4-Dibromophenyl Benzoate.*—The benzoate was added slowly to 10 parts of nitric acid (*d* 1.5), kept below 30°. After a further 15 minutes, the solution was poured into excess of cold water. The gummy precipitate was separated, and heated with water until it became hard. It crystallised from alcohol in colourless needles, m. p. 155–156° (Found: Br, 36.2.  $C_{13}H_6O_6N_2Br_2$  requires Br, 35.9%). The nitro-compound was heated for an hour at 100° with excess of piperidine. The excess of piperidine was removed by extraction with benzene in presence of alkali. The 2:4-dibromo-5-nitrophenol obtained, after crystallisation from

light petroleum, had m. p. 77—78°, and did not depress the m. p. of the dibromo-compound described above.

The *m*-nitrophenol used in these experiments was prepared as described in Adams's "Organic Syntheses," Vol. VIII, p. 80, but it was found advisable to remove all traces of sulphuric acid from the crude product by dissolving it in alkali and reprecipitating it with hydrochloric acid before distilling it under reduced pressure; otherwise, towards the end of the distillation, explosive decomposition set in. From 212 g. of *m*-nitroaniline, 135—140 g. of pure *m*-nitrophenol were consistently obtained.

*m*-Nitrophenyl *p*-toluenesulphonate, obtained in the usual way, separated from alcohol in prisms, m. p. 112—113° (Found: S, 10.7.  $C_{13}H_{11}O_5NS$  requires S, 10.9%).

*Experiments on the Dibromination of m-Nitrophenol.*—(A) *Dry*. (1) The method described by Lindner (*loc. cit.*) led to mixtures, the examination of which proved unprofitable.

(2) A current of carbon dioxide laden with bromine vapour was passed through *m*-nitrophenol in a bath at 120—140° until the desired increase in weight had occurred. The product was worked up by Lindner's method. Precipitation of the barium-salt fraction gave a solid, m. p. 82—98°. A mixture of this with 2 : 4 : 6-tribromo-3-nitrophenol melted below 75°, and one with 4-bromo-3-nitrophenol melted at 76—135°. On the assumptions that the product, m. p. 82—98°, is approximately 50% of 4-bromo- and 50% of tribromo-3-nitrophenol, and that the mixed melting-point curve is of the simplest type, these results are explicable, as is also the bromine content of the bromination product (51.3%; a 1 : 1 mixture of mono- and tri-bromo-compounds requires Br, 53.9%).

(3) On one occasion, by Schlieper's method of monobromination, a product was obtained corresponding very closely to that just described. It had m. p. 85—95°, and Br, 51.2%.

(B) *Wet*. (1) A solution of *m*-nitrophenol (1 mol.) and bromine (2 mols.) in 90% acetic acid was left in the cold for an hour. Since bromination did not begin, the solution was heated at 100° for 0.5 hour and then boiled for 0.5 hour. The product was worked up by Lindner's method and gave no substance corresponding to his dibromo-derivative.

(2) A solution of *m*-nitrophenol (1 mol.) and anhydrous sodium acetate (2 mols.) in glacial acetic acid was treated with a solution of bromine (2 mols.) in glacial acetic acid. A number of experiments were carried out, with variation of concentrations, temperature, and time of mixing. In every case the main product was 2 : 4 : 6-tribromo-3-nitrophenol, m. p. 89—90° (Found: Br, 63.4. Calc.: Br, 63.8%).

**2 : 4 : 6-Tribromo-3-nitrophenyl p-Toluenesulphonate.**—The tribromo-compound was readily converted into the *p*-toluenesulphonyl derivative, which crystallised from alcohol in colourless needles, m. p. 146—147° (Found : Br, 45·2; S, 6·0.  $C_{13}H_8O_5NBr_3S$  requires Br, 45·3; S, 6·0%).

**2 : 4 : 6-Tribromo-3-aminophenyl p-Toluenesulphonate.**—Reduction of the preceding compound was effected by West's method (J., 1925, 127, 494). The amino-compound separated from alcohol or dilute acetic acid in colourless prisms, m. p. 146—147° (mixture with the nitro-compound, m. p. 120—125°) (Found : Br, 47·9.  $C_{13}H_{10}O_3NBr_3S$  requires Br, 48·0%).

**2 : 3 : 4 : 6-Tetrabromophenol.**—A solution of the preceding amino-compound in concentrated sulphuric acid was diazotised at 15° with a solution of sodium nitrite in concentrated sulphuric acid (made at -10°). When the resulting solution was poured on ice, a yellow crystalline precipitate of the diazo-compound separated. Addition of water produced a clear solution, to which was added a solution of bromine in potassium bromide until no further precipitate was obtained. The diazo-perbromide was collected, washed with water, and decomposed in hot glacial acetic acid. On cooling, a crystalline product separated, which was washed with water and then heated with excess of piperidine at 100° for 4 hours. Addition of water precipitated 2 : 3 : 4 : 6-tetrabromophenol, which soon became solid and crystallised from dilute alcohol in colourless needles, m. p. 113—114°. An identical specimen was obtained by using the Sandmeyer instead of the perbromide process (Found : Br, 76·8. Calc. : Br, 78·0%).

**N-*p*-Bromophenylphthalimide.**—A mixture of *p*-bromoaniline (1 mol.) with finely ground phthalic anhydride (1 mol.) was heated at 250—300° for 2 hours. The molten mass was poured into cold alcohol and the solid product was ground and extracted with a large volume of boiling alcohol. The residual solid and the long silky needles that separated from the extract both melted at 204° (Found : Br, 26·8.  $C_{14}H_8O_2NBr$  requires Br, 26·5%). Yield, 88%.

**Nitration of N-*p*-Bromophenylphthalimide.**—The imide (1 mol.) was dissolved in 10 parts of warm concentrated sulphuric acid. To the solution, cooled in running water, 1 mol. of nitric acid (*d* 1·5), dissolved in 5 vols. of concentrated sulphuric acid, was added slowly, with stirring. After an hour, the solution was poured on ice, and the resulting gummy precipitate collected. It was heated for an hour at 130° with 90% sulphuric acid, and the resulting solution was much diluted and then basified. The product was mainly 4-bromo-2-nitroaniline, and did not contain more than 20% of 4-bromo-3-nitroaniline (fractional crystallisation of the mixed sulphates).



Nitration of *p*-bromoaniline in excess of sulphuric acid as described by Noelting and Collin (*loc. cit.*) gave 4-bromo-3-nitroaniline in good yield, but an attempt to effect replacement of the amino-group by hydroxyl by the diazo-method proved unsuccessful.

*Mononitration of ON-Diacetyl-p-aminophenol.*—Hähle (*loc. cit.*) recommends nitration at 0° with fuming nitric acid. We have found that the best results are obtained when 50 g. of the diacetyl compound are added gradually to 75 c.c. of nitric acid (*d* 1.5) kept at about 5°. (Only partial nitration occurs at temperatures just below 0°, and the diacetyl compound may be recovered unchanged from its solution in a mixture of equal volumes of acids of *d* 1.5 and *d* 1.42, kept at 0° to -5°.) The solution is poured on ice, and the precipitate obtained is crystallised from alcohol.

*4-Bromo-3-nitrophenol.*—*ON*-Diacetyl-3-nitro-4-aminophenol was slowly added to 10 times its weight of boiling hydrobromic acid (*d* 1.49). Boiling was continued for  $\frac{1}{2}$  hour and the suspension of 3-nitro-4-aminophenol hydrobromide was then diluted and diazotised: diazotisation was slow. The excess of nitrous acid was removed by addition of urea and the solution obtained was poured into a suspension of copper powder in 25% hydrobromic acid. The copper slowly dissolved and needles separated. These crystallised from water in brown needles, *m. p.* 146.5—147.5°, and from dilute hydrochloric acid in yellow needles having the same *m. p.*

4-Chloro-3-nitrophenol was obtained in a precisely similar manner from diacetyl-3-nitro-4-aminophenol. The diazotisation proceeded more easily than with the bromo-compound. The product crystallised from dilute hydrochloric acid in yellow needles, *m. p.* 127—128°.

3-Bromo-2-nitrophenol was prepared by Hodgson and Moore's method (*J.*, 1926, 157). In the intermediate sulphonation we obtained good results with 20% oleum, but with acid of the composition (27% oleum) used by Hodgson and Moore, our sulphonation mixture set almost solid and would not dissolve even in a large quantity of concentrated sulphuric acid.

3-Bromo-2-nitrophenyl *p*-toluenesulphonate, readily obtained in the usual way, crystallised from alcohol, in which it was very sparingly soluble, in colourless rectangular plates, *m. p.* 136.5—137.5° (Found: Br, 21.4.  $C_{13}H_{10}O_5NBrS$  requires Br, 21.5%).

3-Bromo-2-aminophenyl *p*-Toluenesulphonate.—The preceding nitro-compound was reduced with a mixture of 2 parts of crystalline stannous chloride, 2 parts of concentrated hydrochloric acid, and 7 parts of glacial acetic acid at 100°. Much alkali was added and the suspension produced was extracted with ether. Evaporation of the dried ethereal extract, followed by crystallisation from alcohol,

gave colourless needles of the *amino*-compound, m. p. 120—121° (Found: Br, 23·6.  $C_{13}H_{12}O_3NBrS$  requires Br, 23·4%).

**2:3-Dibromophenol.**—The *amino*-compound was diazotised in concentrated sulphuric acid at 15—20°, with a solution of sodium nitrite in concentrated sulphuric acid prepared at -10°. The reaction mixture was poured on ice. A small portion was found to couple normally with alkaline  $\beta$ -naphthol, and the main portion was added to cuprous bromide-hydrobromic acid. The resulting solution was heated on a boiling water-bath under reflux for  $\frac{3}{4}$  hour and then distilled in steam. The white solid that passed over was dried over concentrated sulphuric acid (desiccator) and crystallised from light petroleum (b. p. 40—60°). The 2:3-dibromophenol obtained formed stout prisms, m. p. 68—69° (Found: Br, 63·6.  $C_6H_4OBr_2$  requires Br, 63·6%). It is much less soluble in light petroleum than 2:3-dichlorophenol and is very much less volatile.

**Monobromination of Wet m-Nitrophenol.**—(a) When a dilute solution of bromine (1 mol.) was added to a cold dilute solution of *m*-nitrophenol (1 mol.) and anhydrous sodium acetate (1 mol.) in glacial acetic acid, a mixture of substances was formed, the examination of which led to no positive results.

(b) A solution of 20 g. of *m*-nitrophenol and 8·8 c.c. of bromine in 30 c.c. of glacial acetic acid was gently boiled under reflux for 2 hours; it then became almost colourless. The solvent was evaporated on a boiling water-bath and the residue, which became crystalline on cooling, was dissolved in dilute aqueous alkali. Addition of acid precipitated an almost colourless solid which, after being crystallised from dilute hydrochloric acid, melted at 117—120°, and after a further crystallisation from light petroleum (b. p. 80—100°), at 118·5—121° (Found: Br, 36·4.  $C_6H_4O_3NBr$  requires Br, 36·7%). The following experiments show that this substance is 2-bromo-5-nitrophenol.

2-Bromo-5-nitrophenyl *p*-toluenesulphonate was formed in good yield by the usual process; it crystallised from alcohol in colourless plates, m. p. 131·5—132·5° (Found: Br, 21·6.  $C_{13}H_{10}O_5NBrS$  requires Br, 21·5%).

2-Bromo-5-aminophenyl *p*-toluenesulphonate, obtained by the reduction of the nitro-compound with stannous chloride, hydrochloric acid, and acetic acid, crystallised from alcohol in colourless bunches of prisms, m. p. 135—136° (Found: Br, 23·3.  $C_{13}H_{12}O_3NBrS$  requires Br, 23·4%).

**2:5-Dibromophenol.** (a) The last-named *amino*-compound was diazotised in concentrated sulphuric acid exactly as described under the preparation of 2:3-dibromophenol. The steam-distilled 2:5-dibromophenol was dried over concentrated sulphuric acid

(desiccator) and then crystallised from light petroleum (b. p. 40—60°); it formed prismatic needles, m. p. 73—74° (Found: Br, 63.4.  $C_6H_4OBr_2$  requires Br, 63.6%). It was readily converted into 2:5-dibromophenyl *p*-toluenesulphonate, which separated from alcohol in colourless prisms, m. p. 109—110° (Found: Br, 39.7.  $C_{13}H_{10}O_3Br_2S$  requires Br, 39.4%).

(b) 2:5-Dibromoaniline (44 g.), obtained in good yield by reducing 2:5-dibromonitrobenzene by West's method, was dissolved in 150 c.c. of warm concentrated sulphuric acid. The solution was cooled to room temperature and treated with a solution of 13 g. of sodium nitrite in 150 c.c. of concentrated sulphuric acid (prepared at -10°). After an hour, 150 c.c. of water were added and the resulting solution, after addition of purified sand, was heated under reflux over a small flame for 2 hours. (A small portion of the diluted diazo-solution coupled readily with alkaline  $\beta$ -naphthol.) The whole was then distilled in steam, 37 g. of 2:5-dibromophenol, containing a trace of 2:5-dibromoaniline, passing over. The phenol was freed from the base by solution in alkali and filtration and then recovered by acidification; it had m. p. 73—74°, b. p. 256—257° (corr.)/755 mm. The *p*-toluenesulphonyl derivative melted at 109—110°.

Mixtures of the phenols or of their *p*-toluenesulphonyl derivatives obtained by methods (a) and (b) had the same m. p. as those of the single substances.

*Monobromination of Dry m-Nitrophenol.*—(1) A current of dry carbon dioxide was passed through bromine and then through 10.5 g. of *m*-nitrophenol heated at 120—140°. When the calculated increase of weight had occurred, the product was freed from the excess of bromine by a rapid current of carbon dioxide and at once dissolved in excess of dilute sodium hydroxide solution. After addition of dilute hydrochloric acid, yellow needles of 4-bromo-3-nitrophenol separated for some time, and later, an oil made its appearance. At this stage the liquid was filtered and the solid was crystallised from dilute hydrochloric acid, 7 g. of the 4-bromo-compound, m. p. 146.5—147.5°, being obtained.

(2) *m*-Nitrophenol (28 g.) was brominated, the weight being allowed to increase to 43 g. When the product was worked up as before, 22 g. of pure 4-bromo-3-nitrophenol were obtained.

The products from both experiments did not depress the m. p. of 4-bromo-3-nitrophenol prepared from diacetyl-*p*-aminophenol.

*Attempted Monobromination of 4-Bromo-3-nitrophenol.*—When the monobromo-compound (1 mol.), dissolved together with 1 mol. of anhydrous sodium acetate in glacial acetic acid, was treated with 1 mol. of bromine dissolved in the same solvent, a mixture was obtained containing unchanged 4-bromo-3-nitrophenol.

*Attempted Monobromination of 2-Bromo-5-nitrophenol.*—This appeared to proceed readily. The acetic acid was evaporated, and the hard solid obtained (on cooling) crystallised from light petroleum (b. p. 80—100°). The product had the appearance of an individual substance, but melted at 68—108°.

*Monochlorination of m-Nitrophenol.*—Chlorine was passed into *m*-nitrophenol (42 g.) at 120—140° until the weight increased by 9.5 g. A rapid current of carbon dioxide was passed through the molten product until the excess of chlorine had disappeared and the whole was then dissolved in dilute alkali solution. Dilute hydrochloric acid was added until no further evident precipitation occurred and the yellow needles produced were washed and dried (14 g.). After crystallisation from dilute hydrochloric acid, 12 g. of pure 4-chloro-3-nitrophenol, m. p. 127—128°, were obtained. The mother-liquor from the first filtration was strongly acidified, and filtered after some time: the yellow precipitate obtained, having been washed and dried, weighed 16 g. and after crystallisation from dilute hydrochloric acid gave 10 g. of 2-chloro-3-nitrophenol, m. p. 120° (Found: Cl, 19.6. Calc.: Cl, 20.0%). The mother-liquor from the second precipitation was evaporated to a small bulk under reduced pressure and then extracted with ether. Evaporation of the extract gave 12.5 g. of an oily mixture of chloro-compounds. The total yield of crude chloro-compounds was 85% of the theoretical yield.

The 4-chloro-3-nitrophenol obtained produced no depression of the m. p. of the material prepared from *ON*-diacetyl-*m*-nitro-*p*-aminophenol.

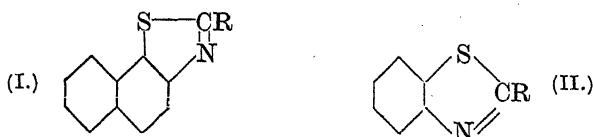
The 2-chloro-3-nitrophenol was reduced with iron, hydrochloric acid, and alcohol, and the filtered solution evaporated to dryness. Diazotisation, followed by addition of copper powder and hydrochloric acid, gave 2:3-dichlorophenol, m. p. 56—57°: this depressed the m. p. of 2:5-dichlorophenol (m. p. 57°). 2:3-Dichlorophenol is extraordinarily volatile, and vacuum desiccation over sulphuric acid and phosphoric oxide was accompanied by considerable loss. This property and the intense odour of the compound appear to differentiate this dichlorophenol from its isomerides (compare Holleman, *Rec. trav. chim.*, 1917, 37, 96), and the volatility accounts for the poor analytical figure obtained (Found in air-dried specimen: Cl, 41.7. Calc.: Cl, 43.6%).

Some of the preliminary work on the dibromodinitrodiphenyl ether was carried out by Miss G. I. Sharp, B.Sc.

CXV.—*The Unsaturation and Tautomeric Mobility of Heterocyclic Compounds. Part II.  $\alpha$ - and  $\beta\beta$ -Naphthathiazoles.*

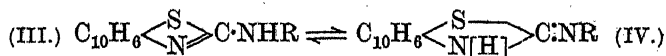
By ROBERT FERGUS HUNTER and JOHN WILLIAM THOMAS JONES.

RING closure, producing the heterocyclic nucleus in  $\alpha$ -naphthathiazoles (I) and in benzthiazoles (II), takes place much more readily in the former than in the latter case : for instance, (1) the ratio of



the yields of the 1-chloro-derivatives (I and II; R = Cl) obtained from the corresponding arylthiocarbimides and phosphorus pentachloride under similar conditions (Hofmann, *Ber.*, 1879, 12, 1126) is 62 : 15; (2) oxidation of  $\beta$ -naphthylthiourethane and of phenylthiourethane with alkaline ferricyanide at 80–90° gives 60% and 40% yields, respectively, of the corresponding ethoxythiazoles (I and II; R = OEt) (Jacobson, *Ber.*, 1886, 19, 1069); and (3) the action of bromine on *s*-phenyl- $\beta$ -naphthylthiocarbamide yields solely 1-anilino- $\alpha$ -naphthathiazole (I; R = NHPh), no trace of the isomeric 1- $\beta$ -naphthylaminobenzthiazole (II; R = NH·C<sub>10</sub>H<sub>7</sub>), which has been synthesised from 1-chlorobenzthiazole and  $\beta$ -naphthylamine, being isolable. These results are evidently conditioned by the high reactivity of the  $\alpha$ -hydrogen atom of the naphthalene nucleus.

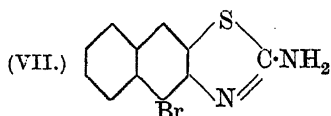
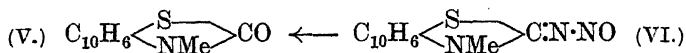
The aromatic nature of the heterocyclic nucleus in  $\alpha$ -naphthathiazole is manifested in the alkylation of semi-cyclic amidines containing this complex (III  $\rightleftharpoons$  IV). For instance, the methyl-



ation of 1-amino- $\alpha$ -naphthathiazole (III; R = H) yields 1-imino-2-methyl-1 : 2-dihydro- $\alpha$ -naphthathiazole, unaccompanied by the isomeric 1-methylamino- $\alpha$ -naphthathiazole (compare Hunter, *J.*, 1926, 1385; Hunter and Styles, *J.*, 1928, 3019). 1- $\beta$ -Naphthylamino- $\alpha$ -naphthathiazole (III; R = C<sub>10</sub>H<sub>7</sub>) behaves similarly and yields only 1- $\beta$ -naphthylimino-2-methyl-1 : 2-dihydro- $\alpha$ -naphthathiazole on methylation, although it contains the  $\beta$ -naphthyl group which might exert a conjugating influence favouring the iminodihydro-phase (IV), similar to that of the phenyl group in the three-carbon system (Linstead and Williams, *J.*, 1926, 2735; Linstead, *J.*, 1929, 2501). The isomeric 1-methyl- $\beta$ -naphthylamino- $\alpha$ -naphthathiazole has been

obtained from 1-chloro- $\alpha$ -naphthathiazole and methyl- $\beta$ -naphthylamine and also by the action of bromine on methyl-*s*-di- $\beta$ -naphthylthiocarbamide,  $C_{10}H_7 \cdot NMe \cdot CS \cdot NH \cdot C_{10}H_7$ .

The methylation of 1-hydroxy- $\alpha$ -naphthathiazole is analogous to that of 1-hydroxybenzthiazole (Hunter, this vol., p. 128), the sole product being the ketomethyldihydro-derivative (V), whose constitution follows from its synthesis from 1-nitrosoimino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole (VI).



3-Bromo-1-amino- $\beta\beta$ -naphthathiazole (VII) has been obtained from 1-bromo- $\beta$ -naphthylamine by way of the thiocarbimide and thiocarbamide in the usual way (compare Fries, *Annalen*, 1927, 454, 260).

#### EXPERIMENTAL.

Considerable difficulty was encountered in preparing  $\beta$ -naphthylthiocarbimide by the methods given in the literature. It was most readily obtained by boiling a mixture of *s*-di- $\beta$ -naphthylthiocarbamide (50 g.) and acetic anhydride (100 c.c.) for 3 minutes, diluting the solution with hot water, and isolating the thiocarbimide by prolonged distillation in steam superheated to  $140^\circ$ . The yield never exceeded 30%. The thiocarbimide to be used for the preparation of the chloronaphthathiazole was melted over calcium chloride and redistilled in a vacuum, the fraction, b. p.  $182\text{--}184^\circ/12$  mm., being separately collected.

1-Chloro- $\alpha$ -naphthathiazole.—A mixture of 14 g. of  $\beta$ -naphthylthiocarbimide and phosphorus pentachloride (16 g.) was heated in a sealed tube at  $160\text{--}180^\circ$  for 5–6 hours, and the product fractionated. After removal of phosphorus trichloride and a small quantity of unchanged thiocarbimide ( $183^\circ/15$  mm.), the chlorothiazole distilled at  $260\text{--}270^\circ/15$  mm. The yield after redistillation and crystallisation from alcohol was 62%; m. p.  $80^\circ$ , b. p.  $245\text{--}246^\circ/13$  mm. (Found: Cl, 16.0; S, 14.8.  $C_{11}H_6NCIS$  requires Cl, 16.1; S, 14.5%).

1-Hydroxy- $\alpha$ -naphthathiazole.—A solution of the chloronaphthathiazole (0.8 g.) in absolute alcohol (20 c.c.) was diluted with 4 c.c. of concentrated hydrochloric acid, heated for 20 hours under reflux, and evaporated on a steam-bath. On recrystallisation from alcohol, the hydroxy-base formed aggregates of shining prisms, m. p.  $230\text{--}$

231° (Found: S, 16.2.  $C_{11}H_7ONS$  requires S, 15.9%). This compound is less soluble in alkalis than the benzthiazole analogue.

*1-Amino- $\alpha$ -naphthathiazole*.—Although Hofmann states (*Ber.*, 1879, **12**, 1126) that 1-aminobenzthiazole is obtained by digesting 1-chlorobenzthiazole with alcoholic ammonia at 100°, the chloro-naphthathiazole was recovered unchanged under such conditions, and also after being heated in a sealed tube (0.5 g. of the chloro-base) with alcoholic ammonia (5 c.c. of alcohol and 2 c.c. of ammonia,  $d$  0.880) at 100–140° for  $\frac{1}{2}$  hour.

(i) A mixture of 0.5 g. of 1-chloro- $\alpha$ -naphthathiazole and 5 c.c. of ammonia ( $d$  0.880) was heated at 200° for 18 hours. On recrystallisation from alcohol, 1-amino- $\alpha$ -naphthathiazole was obtained, m. p. 258° alone and when mixed with the specimen prepared from  $\beta$ -naphthylthiocarbamide (previously given, *J.*, 1926, 1400, as m. p. 249–251°; the compound is there erroneously named “2-amino- $\alpha$ -naphthathiazole”). The identity was further confirmed by the formation of the same acetyl derivative. (ii) Treatment of a suspension of  $\beta$ -naphthylthiocarbamide (m. p. 194°; Cosiner, *Ber.*, 1881, **14**, 59, recorded m. p. 180°, and Hector, *Ber.*, 1890, **23**, 362, m. p. 186°) (1 g.) in chloroform (10 c.c.) with bromine (1 c.c. in 1 c.c. of chloroform) yielded a yellow *hydrotribromide*, which sintered at 160–161° after drying in a vacuum [Found: Br, 54.8.  $C_{11}H_8N_2S \cdot HBr(Br_2)$  requires Br, 54.4%]. On reduction with sulphurous acid, basification with ammonia, and recrystallisation from methyl alcohol, this gave the aminonaphthathiazole in plates, m. p. 257° (Found: S, 16.2. Calc.: S, 16.0%).

*1-Acetamido- $\alpha$ -naphthathiazole*.—(i) The product of acetylation of the amino-base with acetic anhydride separated from benzene-ethyl acetate in soft crystals, m. p. 265° (Found: S, 12.9.  $C_{13}H_{10}ON_2S$  requires S, 13.2%).

Hugershoff (*Ber.*, 1899, **32**, 3649) states that treatment of  $\beta$ -naphthylthiocarbamide with acetic anhydride at 80° yields *as*-acetyl- $\beta$ -naphthylthiocarbamide,  $C_{10}H_7 \cdot NAc \cdot CS \cdot NH_2$ , which isomerises to *s*-acetyl- $\beta$ -naphthylthiocarbamide,  $C_{10}H_7 \cdot NH \cdot CS \cdot NHAc$ , m. p. 158°, at its melting point. The product which we isolated from  $\beta$ -naphthylthiocarbamide and acetic anhydride at 80° had m. p. 145–147° and proved to be a mixture containing unchanged naphthylthiocarbamide. On the other hand, *s*-acetyl- $\beta$ -naphthylthiocarbamide was readily prepared by dissolving  $\beta$ -naphthylthiocarbamide in an excess of acetic anhydride at 80° (compare Hunter and Pride, *J.*, 1929, 944); it melted at 171–172° after recrystallisation.

(ii) The solution obtained from 0.3 g. of *s*-acetyl- $\beta$ -naphthylthiocarbamide, 6 c.c. of chloroform, and 0.5 c.c. of bromine was heated

under reflux for 2 minutes, and the orange bromo-addition compound (m. p. 154—156°) obtained was reduced with sulphurous acid. On recrystallisation from boiling alcohol, the acetamidonaphthathiazole formed plates, m. p. 264° alone and when mixed with the specimen obtained in (i).

*1-Ethoxy- $\alpha$ -naphthathiazole*.—10 G. of  $\beta$ -naphthylthiourethane (m. p. 96°; prepared in 95% yield by heating a solution of the thiocarbimide in absolute alcohol, containing a few drops of quinoline, under reflux for 4 hours) were rubbed with a small quantity of alcohol and dissolved in 75 c.c. of 30% aqueous sodium hydroxide. The solution was diluted with water to 200 c.c. and added in 20 c.c. portions at 5-minute intervals to 300 c.c. of a well-stirred 20% solution of potassium ferricyanide at 85°; the cooled mixture was extracted with ether, and the product recrystallised from alcohol (yield, 5.9 g.; 60%). The *ethoxy-base* formed needles, m. p. 80° (Found: S, 14.1.  $C_{13}H_{11}ONS$  requires S, 14.0%).

*Hydrolysis*. 1-Ethoxy- $\alpha$ -naphthathiazole (1 g.) was heated with 7 c.c. of hydrobromic acid (*d* 1.45) for 15 minutes; the mixture was diluted with water (10 vols.), and the product recrystallised from alcohol-ethyl acetate (animal charcoal), 0.4—0.5 g. of 1-hydroxy- $\alpha$ -naphthathiazole being obtained, m. p. 231° alone and when mixed with the specimen obtained from the chloronaphthathiazole.

*1-Ethoxybenzthiazole*.—A similar experiment with 10 g. of phenylthiourethane gave 4 g. of 1-ethoxybenzthiazole (yield, 40%), which was characterised by its hydrolysis to 1-hydroxybenzthiazole, m. p. 138° (Hunter, this vol., p. 135).

*1- $\beta$ -Naphthylaminobenzthiazole*.—When a mixture of 1-chlorobenzthiazole (1 g.) and  $\beta$ -naphthylamine (0.8 g.) was heated, a vigorous reaction took place. The product was extracted with alcohol, the extracts were decolorised with animal charcoal and evaporated on a steam-bath, and the residue was basified and recrystallised from methyl alcohol-ethyl acetate. The *naphthylaminobenzthiazole* (yield, 60%) formed small silky needles, m. p. 191—192° (Found: S, 11.8.  $C_{17}H_{12}N_2S$  requires S, 11.6%). The acetyl derivative could not be crystallised.

*1-Anilino- $\alpha$ -naphthathiazole*.—The tenacious gum obtained by condensing 1-chloro- $\alpha$ -naphthathiazole (1 g.) with aniline (0.5 c.c.) solidified on treatment with hot aqueous ammonia (*d* 0.880). On recrystallisation from methyl alcohol-ethyl acetate, 1-anilino- $\alpha$ -naphthathiazole was obtained in soft silky needles, m. p. 211—212° (Found: S, 11.7.  $C_{17}H_{12}N_2S$  requires S, 11.6%).

*Condensation of Phenylthiocarbimide with  $\beta$ -Naphthylamine*.—6.5 C.c. of phenylthiocarbimide were added to a boiling solution of 7 g. of  $\beta$ -naphthylamine in absolute alcohol (70 c.c.); the mixture



became semi-solid owing to the separation of the phenylnaphthylthiocarbamide (yield, 13 g.; m. p. 161—162°). On recrystallisation from ethyl acetate and thereafter from amyl acetate, *s*-phenyl- $\beta$ -naphthylthiocarbamide was obtained in silvery plates, m. p. 166—167° (Found: S, 11.8. Calc.: S, 11.6%). Mainzer (*Ber.*, 1882, 15, 1471), Freund and Wolf (*Ber.*, 1892, 25, 1468), and Wheeler (*J. Amer. Chem. Soc.*, 1901, 33, 226) give the m. p. as 157°, 165°, and 182—183°, respectively.

*Condensation of  $\beta$ -Naphthylthiocarbimide with Aniline.*—Owing to the readiness with which  $\beta$ -naphthylthiocarbimide combines with alcohol in the presence of amines, this condensation was carried out in benzene solution. After recrystallisation, the product had m. p. 166°, alone and when mixed with the phenylnaphthylthiocarbamide described above.

*Wheeler's "Phenylnaphthylthiocarbamide."*—A mixture of 1 g. of  $\beta$ -naphthylamine and 1.5 c.c. of phenylthiocarbimide was heated until it boiled; the product, which solidified on cooling, was recrystallised from amyl acetate. It formed ill-defined crystals, m. p. 182—184° (softening at 175°), and m. p. 188—189° after extraction with boiling alcohol, in which it was very sparingly soluble. From its properties and the m. p. of its mixture with a genuine specimen (m. p. 193—195°), Wheeler's product (*loc. cit.*) was evidently *s*-di- $\beta$ -naphthylthiocarbamide. Its mixture with a genuine specimen of *s*-phenyl- $\beta$ -naphthylthiocarbamide melted at 158—159°.

It appears probable that *s*-phenyl- $\beta$ -naphthylthiocarbamide is formed initially in Wheeler's experiment and then undergoes decomposition at the elevated temperature attained during the condensation. This supposition is borne out by the following experiment.

*Thermal Decomposition of s-Phenyl- $\beta$ -naphthylthiocarbamide.*—1 G. of the thiocarbamide was kept at 220—230° for 2 minutes, hydrogen sulphide being evolved. The product, which crystallised on cooling, was repeatedly extracted with boiling alcohol, finely ground, and re-extracted with boiling alcohol and thereafter with ethyl acetate. The residue melted at 191—193°, and at 192—194° when mixed with a genuine specimen of *s*-di- $\beta$ -naphthylthiocarbamide.

The alcoholic extracts yielded *s*-phenyl- $\beta$ -naphthylthiocarbamide and some phenylthiocarbimide on evaporation, but the presence of thiocarbimide could not be detected.

*The Action of Bromine on s-Phenyl- $\beta$ -naphthylthiocarbamide.*—A suspension of 3 g. of the thiocarbamide in 30 c.c. of chloroform was treated with bromine (1.2 c.c. in 3 c.c. of chloroform) (an excess of bromine, such as is normally used in the Hegershoff reaction, causes

the production of ill-defined bromo-substitution derivatives) and the mixture was heated under reflux for 3 minutes, cooled, and evaporated to dryness under reduced pressure at laboratory temperature. The product was dissolved in chloroform, the solution shaken with sulphurous acid, and the reduction completed by passage of sulphur dioxide. On basification and removal of the chloroform, a base, m. p. 202—205°, was obtained which on recrystallisation from ethyl acetate yielded 2.2 g. of 1-anilino- $\alpha$ -naphthathiazole, m. p. 206—211°. The mother-liquor furnished a further 0.7 g. of the same base (m. p. ca. 200°). On recrystallisation both fractions had m. p. 211°, alone and when mixed with the specimen of 1-anilino- $\alpha$ -naphthathiazole obtained from 1-chloro- $\alpha$ -naphthathiazole (p. 944). No trace of the isomeric naphthylaminobenzthiazole was found.

1-*p*-Bromoanilino- $\alpha$ -naphthathiazole, which could not be obtained by the bromination of 1-anilino- $\alpha$ -naphthathiazole in chloroform, was prepared by the condensation of 1-chloro- $\alpha$ -naphthathiazole and *p*-bromoaniline; it formed small prisms, m. p. 250° (Found: Br, 22.8.  $C_{17}H_{11}N_2BrS$  requires Br, 22.5%).

*Methylation of 1-Amino- $\alpha$ -naphthathiazole and the Synthesis of 1-Imino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole and of 1-Methyl-amino- $\alpha$ -naphthathiazole from the Corresponding Naphthylmethylthiocarbamides.*—A mixture of 1-amino- $\alpha$ -naphthathiazole (2.6 g.) and methyl iodide (3 c.c.) was heated in a sealed tube at 100° for 15 hours. The product was basified with alcoholic potash and the mixture was diluted with water and extracted with ethyl acetate, 1.45 g. of 1-imino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole, m. p. 178°, being obtained (Found: S, 15.0.  $C_{12}H_{10}N_2S$  requires S, 14.9%) unaccompanied by any trace of the 1-methylamino-isomeride.

Methyl- $\beta$ -naphthylamine was conveniently prepared as follows: Sodium (1 atom) was dissolved in a hot solution of aceto- $\beta$ -naphthalide (20 g.) in xylene (200 c.c.). After 15 minutes, crystallisation commenced, methyl sulphate (30 c.c.) was added to the semi-solid mass, and the mixture heated for 5 minutes. The xylene was then distilled in steam, and the product heated with alcoholic potash for 24 hours; the alcohol was evaporated on a steam-bath, and the mixture diluted with water and extracted with ether. Distillation of the residue obtained after removal of the ether yielded 8.5 g. of the methylnaphthylamine, b. p. 189°/30 mm. (yield, 50%).

*as- $\beta$ -Naphthylmethylthiocarbamide*, prepared from the methylnaphthylamine, hydrochloric acid, and potassium thiocyanate at 100° (compare Hunter and Styles, J., 1928, 3025), separated from ethyl acetate in small crystals, m. p. 170° (Found: S, 14.7.  $C_{12}H_{12}N_2S$  requires S, 14.8%).

*Reaction with bromine.* A solution of *as- $\beta$ -naphthylmethylthio-*

carbamide (0.5 g.) in chloroform (5 c.c.) was treated with bromine (0.2 c.c. in 2 c.c. of chloroform) and the mixture was heated under reflux for 10 minutes and then shaken with excess of sulphurous acid. The chloroform was evaporated on a steam-bath, and the product basified and recrystallised from alcohol-ethyl acetate, giving 1-imino-2-methyl-1 : 2-dihydro- $\alpha$ -naphthathiazole, identical with the specimen already described.

*s*- $\beta$ -Naphthylmethylthiocarbamide, prepared by condensing  $\beta$ -naphthylthiocarbimide with methylamine in hot alcoholic solution, crystallised in large prisms, m. p. 130° (Found : S, 15.6%).

1-Methylamino- $\alpha$ -naphthathiazole, prepared as in the case of the isomeric iminomethylidihydronaphthathiazole, crystallised in small needles, m. p. 189° (Found : S, 14.7%).

1- $\beta$ -Naphthylamino- $\alpha$ -naphthathiazole, prepared by condensing  $\beta$ -naphthylamine with 1-chloro- $\alpha$ -naphthathiazole, had m. p. 222° alone and when mixed with a specimen prepared from *s*-di- $\beta$ -naphthylthiocarbamide (Hunter, J., 1925, 127, 2270). It is most conveniently prepared from the dinaphthylthiocarbamide in the same way as 1-anilino- $\alpha$ -naphthathiazole is obtained from *s*-phenyl- $\beta$ -naphthylthiocarbamide (p. 945).

*Methylation of 1- $\beta$ -Naphthylamino- $\alpha$ -naphthathiazole.*—The paste obtained from 1 g. of 1- $\beta$ -naphthylamino- $\alpha$ -naphthathiazole and 3 c.c. of chloroform was suspended in 50 c.c. of water containing 10 g. of potassium hydroxide and well shaken with 5 c.c. of methyl sulphate, and again after addition of a further 5 g. of potassium hydroxide and 5 c.c. of methyl sulphate; after  $\frac{1}{2}$  hour the mixture was boiled to remove the chloroform. Recrystallisation of the product from alcohol yielded 1 g. of 1- $\beta$ -naphthylimino-2-methyl-1 : 2-dihydro- $\alpha$ -naphthathiazole (Found : S, 9.5.  $C_{22}H_{16}N_2S$  requires S, 9.4%), unaccompanied by 1-methyl- $\beta$ -naphthylamino- $\alpha$ -naphthathiazole.

*Synthesis of 1-Methyl- $\beta$ -naphthylamino- $\alpha$ -naphthathiazole from Methyl-*s*-di- $\beta$ -naphthylthiocarbamide and from 1-Chloro- $\alpha$ -naphthathiazole and Methyl- $\beta$ -naphthylamine.*—Methyl-*s*-di- $\beta$ -naphthylthiocarbamide, prepared by condensation of  $\beta$ -naphthylthiocarbimide and methyl- $\beta$ -naphthylamine in alcohol, crystallised in soft white plates, m. p. 178° (Found : S, 9.5.  $C_{22}H_{18}N_2S$  requires S, 9.4%).

A solution of this thiocarbamide (0.3 g.) in chloroform (4 c.c.) was treated with 1.6 c.c. of a 10% solution of bromine in the same solvent and the mixture was heated under reflux for 5 minutes, cooled, reduced with sulphurous acid, and basified. On recrystallisation from ethyl acetate, 1-methyl- $\beta$ -naphthylamino- $\alpha$ -naphthathiazole formed shining prisms, m. p. 235° (Found : S, 9.2.  $C_{22}H_{16}N_2S$  requires S, 9.4%). The picrate, prepared from acetone solutions of

the base and picric acid, formed yellow prisms, m. p. 278°, identical with the picrate described below (mixed m. p. 281°).

A mixture of 0.3 g. of 1-chloro- $\alpha$ -naphthathiazole and an equal quantity of methyl- $\beta$ -naphthylamine was heated; on basification an uncrystallisable gum was obtained, which was converted into the picrate, yellow prisms, m. p. 282°, in the usual way (Found: S, 5.6.  $C_{22}H_{16}N_2S, C_6H_3O_7N_3$  requires S, 5.6%).

*Methylation of 1-Hydroxy- $\alpha$ -naphthathiazole and the Synthesis of 1-Keto-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole from 1-Imino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole.*—A solution of 0.5 g. of 1-hydroxy- $\alpha$ -naphthathiazole in 5 c.c. of chloroform was shaken with 6 c.c. of 30% potassium hydroxide solution and 4 c.c. of methyl sulphate, the mixture was heated under reflux for 5 minutes, a further 2 g. of potassium hydroxide and 2 c.c. of methyl sulphate were added, and the heating was continued for a short time. On removal of the chloroform, 1-keto-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole was obtained in long needles, m. p. 135–136° (Found: S, 15.2.  $C_{12}H_9ONS$  requires S, 14.9%).

1-Nitrosoimino-2-methyl-1:2-dihydro- $\alpha$ -naphthathiazole, prepared from the 1-imino-compound in glacial acetic acid and sodium nitrite (compare Hunter, this vol., p. 145), formed small orange-yellow crystals, which exploded at 165° (Found: S, 12.8.  $C_{12}H_9ON_3S$  requires S, 13.2%).

When the nitrosoimino-compound was heated in xylene until nitrogen ceased to be evolved, and the product crystallised from methyl alcohol, the keto-compound described above was obtained.

*Synthesis of 3-Bromo-1-amino- $\beta\beta$ -naphthathiazole.*—A solution of 3 g. of 1-bromo- $\beta$ -naphthylamine in 20 c.c. of chloroform was gradually added with continuous shaking to a suspension of thiocarbonyl chloride (1.5 c.c.) in water (10 c.c.). After  $\frac{1}{2}$  hour the chloroform and the excess of thiocarbonyl chloride were removed, on a steam-bath, through a fractionating column; the 1-bromo- $\beta$ -naphthylthiocarbimide, rapidly crystallised from alcohol, formed small crystals (1.2 g.), m. p. 90° (Found: Br, 29.5.  $C_{11}H_6NBrS$  requires Br, 30.3%).

1-Bromo- $\beta$ -naphthylthiocarbamide, prepared from the thiocarbimide and ammonia in alcoholic solution, formed white plates, m. p. 204° (Found: Br, 28.5.  $C_{11}H_9N_2BrS$  requires Br, 28.5%).

A suspension of 1 g. of the thiocarbamide in chloroform (10 c.c.) was heated under reflux with 1 c.c. of bromine for 10 minutes; the bromo-addition compound which separated was reduced with sulphurous acid. The 3-bromo-1-amino- $\beta\beta$ -naphthathiazole separated from ethyl acetate in small prisms, m. p. 250° (Found: Br, 28.8.  $C_{11}H_7N_2BrS$  requires Br, 28.7%). The acetyl derivative, obtained

from the base and acetic anhydride in the usual way, formed small needles, m. p.  $289^{\circ}$  (Found: S, 10.0.  $C_{13}H_9ON_2BrS$  requires S, 10.0%).

The authors wish to express their gratitude to Professor J. F. Thorpe, F.R.S., for his interest in this work, and to the Trustees of the Dixon Fund of the University of London for grants which have defrayed the cost of the materials.

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### CXVI.—*The Calculation of Activity Coefficients from Solubility Measurements: Thallous Chloride.*

By HERBERT EDWARD BLAYDEN and CECIL WHITFIELD DAVIES

THE study of activities by the method of solubility measurements with a sparingly soluble salt in the presence of other electrolytes has led to the following generalisations: (1) in very dilute solutions the results furnish a striking verification (Brönsted, *Trans. Faraday Soc.*, 1927, 23, 416) of the Debye-Hückel theoretical equation  $-\log f_{\pm} = A\sqrt{\mu}$ , where  $f_{\pm}$  is the mean ion activity coefficient,  $\mu$  is the ionic strength of the solution, and the constant  $A$  has the value 0.505 for a uni-univalent salt in aqueous solution at  $25^{\circ}$ ; (2) at concentrations greater than  $0.01M$ ,  $\log f_{\pm}$  no longer gives a linear relation with  $\sqrt{\mu}$  and depends, moreover, on the nature of the added electrolyte. Thus, Harned (Taylor's "Treatise on Physical Chemistry," 1925, p. 774), speaking of the data on thallous chloride (shown by the series of broken curves in Fig. 2 of this paper), says ". . . the influence of one electrolyte on the activity coefficient of another is a problem of great complexity. Each mixture exhibits individual behavior even in solutions of ionic strength as low as 0.03."

These conclusions are widely accepted, but the figures on which they rest are all based on the assumption that the salts employed are completely dissociated, an assumption which in some instances is invalid. The present paper deals with thallous chloride, the dissociation constant of which is known, and it is shown (1) that in very dilute solutions the value of  $A$  for this salt is much lower than the Debye-Hückel value 0.505, and (2) that when allowance is made for incomplete dissociation, the apparent complexity of the curves disappears, and the activity coefficient is independent of the nature of the other ions present, up to concentrations of  $0.1N$ . Further, this new relationship is shown to be of value for estimating the degree of dissociation of other electrolytes of unknown strength.

*Dissociation Constant of Thallous Chloride.*—The dissociation constant of thallous chloride has been found from conductivity data at 18° to be  $K = 0.31$  (Onsager, *Physikal. Z.*, 1927, **28**, 277) or  $K = 0.30$  (Davies, *Trans. Faraday Soc.*, 1927, **23**, 354). This value has been confirmed by a rather different method (Davies, "Conductivity of Solutions," 1930, p. 141): by evaporating a saturated solution, the Earl of Berkeley (*Phil. Trans.*, 1904, *A*, **203**, 208) found the solubility of the salt to be 0.0132 g.-equiv. per litre (interpolated value at 18°), and by the conductivity method Kohlrausch (*Z. physikal. Chem.*, 1908, **64**, 129) found the value 0.01278 g.-equiv. per litre; the latter figure really represents the ionic concentration of the saturated solution, and the difference between the two values, *viz.*, 0.0004<sub>2</sub>, gives the concentration of undissociated molecules. This agrees very well with the value, 0.00044, calculated from the dissociation constant  $K = 0.30$ .

*Solubility Measurements.*—The solubility of thallous chloride has been measured at 25° in the presence of numerous salts (Noyes, *ibid.*, 1892, **9**, 609; *J. Amer. Chem. Soc.*, 1924, **46**, 1107; Bray and Winninghoff, *ibid.*, 1911, **33**, 1666; Butler and Hiscocks, *J.*, 1926, 2558; Randall and Chang, *J. Amer. Chem. Soc.*, 1928, **50**, 1535). The results in the presence of other univalent chlorides will first be considered, for here the added electrolyte is completely dissociated.

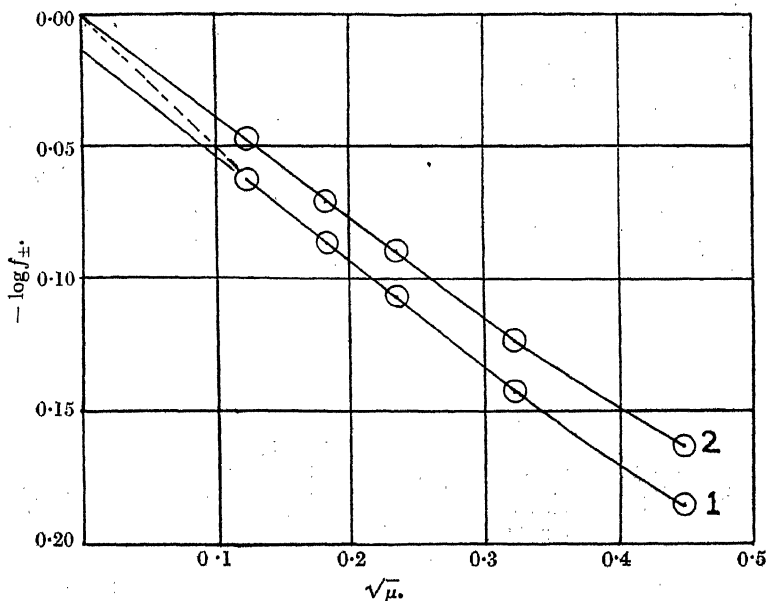
*Solubilities in the Presence of Chlorides of Univalent Metals.*—The degree of dissociation of the pure saturated solution of thallous chloride is first calculated. In the equation  $f_{\pm}^2 c_i^2 / f_u c_u = K$ , where  $c_i$  is the concentration of the ions,  $f_u$  the activity coefficient of the undissociated molecules, and  $c_u$  their concentration, we can put  $K = 0.30$ , and  $f_u$  can be assumed to be equal to unity at low concentrations (compare Randall and Failey, *Chem. Reviews*, 1927, **4**, 291);  $f_{\pm}$  can be calculated from the Debye-Hückel formula by giving  $A$  the value 0.505 as a first approximation, and  $c_i + c_u = 0.01612$ , the solubility of the salt. Solving by successive approximations, we find  $c_i = 0.01552$ ,  $c_u = 0.00060$ ; and for the solubility product,  $S = f_{\pm}^2 \cdot c_i^2 = 18.03 \times 10^{-5}$ .

In a 0.025*N*-potassium chloride solution the solubility of thallous chloride is 0.00872 (Noyes, *loc. cit.*), whence (with  $f_u = 1$ ),  $c_i = 0.00872 - 0.00060 = 0.00812$  and  $f_{\pm}^2 = S / [Cl][Tl] = 18.03 \times 10^{-5} / 0.03312 \times 0.00812 = 0.6708$ , or  $\log f_{\pm} = 1.9133$ . Fig. 1, Curve 1 shows the values calculated in this way for other concentrations of added chloride plotted against the square root of the ionic strength. The points up to 0.1*N* lie on a straight line, the slope of which should give the value of  $A$ , but the extrapolation of this cannot be reconciled with the limiting value  $\log f_{\pm} = 0$  when  $c = 0$ . This, of course, is because the value  $A = 0.505$  was arbitrarily taken in fixing the

position of the first point of the curve, whereas the experimental points lie on a straight line with the slope 0.40. It will be evident that only one value for the factor  $A$  can be consistent both with the corrected solubility values and with the limiting equation  $-\log f_{\pm} = A\sqrt{\mu}$ . This value lies very close to 0.40, and has been found by trial and error to be  $A = 0.38$ .

It is shown below that this same value holds good when the added salt is other than the chloride of a univalent element. In dilute solutions, therefore, the mean ion activity coefficient of thallous

FIG. 1.



chloride varies with the ionic strength of the solution according to the equation  $-\log f = 0.38\sqrt{\mu}$ . Application of this to the conductivity figures used in calculating  $K$  alters  $K$  from 0.30 to 0.284, and similarly the solubility figures give  $S = 19.18 \times 10^{-5}$ . The data recalculated on this basis are given in Table I and are shown in Fig. 1, Curve 2.

*The Value of the Factor A.*—It is of interest to compare the value  $A = 0.38$  with the results for other uni-univalent electrolytes. The Debye-Hückel theory requires the common value 0.505 and the measurements of Brönsted and La Mer (*J. Amer. Chem. Soc.*, 1924, 46, 555) on complex cobalt salts are in striking agreement with this. On the other hand, some of the most accurate experimental investig-

ations have failed to confirm this value. Nonhebel (*Phil. Mag.*, 1926, 2, 1085), from *E.M.F.* measurements, and Randall and Vanselow (*J. Amer. Chem. Soc.*, 1924, 46, 2418), from freezing-point measurements, both find  $A = 0.39$  for hydrochloric acid; further, the value 0.38 has previously been found for several organic acids (Davies, *Phil. Mag.*, 1927, 4, 244). This value might have been regarded as peculiar to the acids, but it now appears to hold also for thallic chloride. For other univalent electrolytes, the data available, although probably less accurate, have led Noyes (*J. Amer. Chem. Soc.*, 1924, 46, 1098) to suggest for them a common  $A$  value of about 0.41. In view of these results—reached by very diverse methods—there seems to be justification for believing that for the simple inorganic ions and some, at least, of the organic anions, the value of the activity factor  $A$  should, in the absence of experimental evidence, be assumed to be 0.39 and not 0.50. Further data alone can show whether  $A$  in reality varies from ion to ion.

*Solubilities in the Presence of Other Salts the Degrees of Dissociation of which are known.*—The data, calculated on the same basis as before, are given in Table I, where the concentrations and solubilities (Sol.) are in g.-equivs. per litre.

TABLE I.

$$S = 19.18 \times 10^{-5}.$$

Conc.	Sol.	$\sqrt{\mu}$ .	$-\log f_{\pm}$ .	Conc.	Sol.	$\sqrt{\mu}$ .	$-\log f_{\pm}$ .
Added salt : KCl, NaCl, $\text{NH}_4\text{Cl}$ (Noyes).				Added salt : $\text{TiNO}_3$ (Noyes).			
0	0.01612	0.1243	0.0472	0.025	0.00883	0.1793	0.0677
0.025	0.00872	0.1818	0.0707	0.050	0.00626	0.2295	0.0925
0.050	0.00592	0.2350	0.0893	0.100	0.00423	0.3076	0.1216
0.100	0.00397	0.3214	0.1241	Added salt : $\text{TiNO}_3$ (Butler and Hiscocks).			
0.200	0.00269	0.4494	0.1628	0.050	0.00615	0.2291	0.0875
Added electrolyte : HCl (Noyes).				0.100	0.00413	0.3071	0.1147
0.025	0.00869	0.1818	0.0718	Added salt : $\text{KNO}_3$ (Bray and Winninghoff).			
0.050	0.00585	0.2349	0.0884	0.020	0.01716	0.1894	0.0722
0.100	0.00384	0.3212	0.1177	0.050	0.01826	0.2558	0.0936
0.200	0.00254	0.4493	0.1488	0.100	0.01961	0.3366	0.1170
Added salts : Bivalent chlorides (Noyes).				0.300	0.02313	0.5406	0.1649
0.025	0.00901	0.2141	0.0824				
0.050	0.00620	0.2838	0.1039				
0.100	0.00467	0.3918	0.1398				
0.200	0.00283	0.5497	0.1805				

The figures for the bivalent chlorides represent the data of Noyes for magnesium, calcium, barium, zinc, manganous, and cupric chlorides, and it has been assumed that these are completely dissociated.

For thallic nitrate the calculations are complicated by the fact



that the added salt is itself incompletely dissociated, so that the solution contains both undissociated thallous chloride and undissociated thallous nitrate. The concentration of undissociated thallous chloride is the same as that in any other solution saturated with respect to this salt, and the concentration of undissociated thallous nitrate is calculated from its dissociation constant,  $K = 0.56$  (Davies, *loc. cit.*), on the assumption that  $A$  has the value 0.38; an error in this assumption would have only a very small effect on the final results, because the concentration of the undissociated nitrate is itself small. Thus, in 0.025*N*-thallous nitrate the solubility of thallous chloride is 0.00883 g.-equiv. per litre (Noyes, *loc. cit.*). Of this quantity, 0.00068 is undissociated molecules, and  $[Cl'] = 0.00815$ . If  $x$  is the concentration of undissociated thallous nitrate,  $[NO'_3] = (0.025 - x)$  and  $[Tl'] = (0.00815 + 0.025 - x)$ ; hence  $f^2 (0.025 - x) (0.03315 - x)/x = 0.56$ , where  $f$ , the mean ion activity coefficient of thallous nitrate is given by  $-\log f = 0.38 \times \sqrt{0.03315 - x}$ , the term under the square-root sign being the ionic strength. By a series of approximations,  $x$  is found to be 0.00101, whence  $[Tl'] = 0.03214$ ,  $f_{\pm}^2 = S/[Cl'][Tl'] = 0.0001918/(0.00815 \times 0.03214)$ , and  $-\log f_{\pm} = 0.0677$ . Similar calculations are applied to the remaining data for thallous nitrate.

When potassium nitrate is the saturating salt, the solution contains three undissociated salts, *viz.*, thallous chloride and nitrate and potassium nitrate ( $K = 1.37$ , Davies, *loc. cit.*). In this case the true concentrations of the ions are calculated by a series of approximations, the method being similar to that just described.

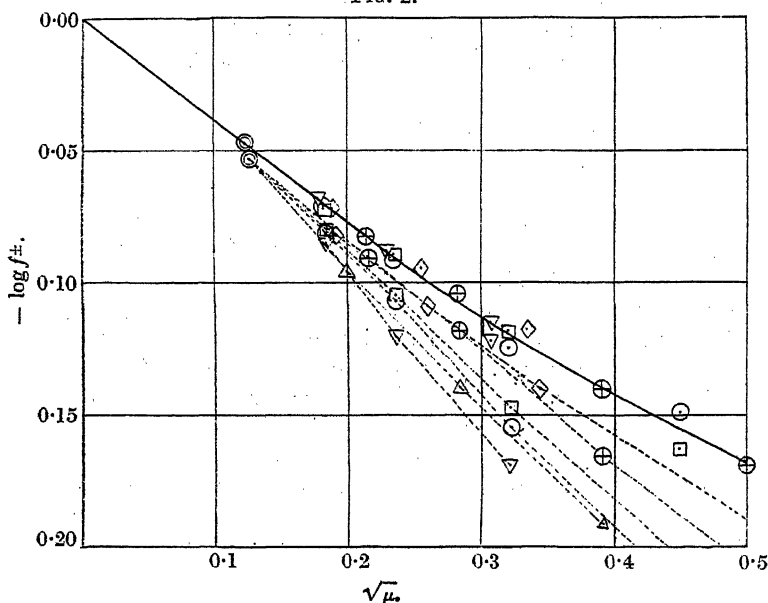
Fig. 2 shows the data for twelve different added salts. The lower series of points, connected by broken lines, is calculated on the assumption that both the thallous chloride and the added salt are completely dissociated; they illustrate the individual differences in behaviour that were formerly believed to exist. The upper series of points, through which a continuous line has been drawn, shows the data as recalculated in this paper. The possible experimental error in the measurements is illustrated by the two bracketed values for the thallous nitrate solution,  $\sqrt{\mu} = 0.308$ ; the lower value was obtained from the figures of Noyes, and the upper from the measurements of Butler and Hiscocks.

The most important conclusion to be drawn is that up to a concentration of about 0.1*N*, the mean ion activity coefficient of thallous chloride depends only upon the ionic strength of the solution and not upon the nature of the other ions present. That the corrections here applied for incomplete dissociation should have so uniformly removed the specific deviations seems, apart from its intrinsic interest, to provide strong support for the dissociation constants derived from

conductivity measurements. It is also noteworthy that the linear relationship between  $\log f_{\pm}$  and  $\sqrt{\mu}$  is found to hold, for thallous chloride at least, up to a higher concentration than 0.01N, the usually accepted limit.

*Solubilities in the Presence of Other Salts.*—If it is accepted that the activity coefficient of thallous chloride, in the more dilute solutions, is dependent only on the ionic strength and not upon the nature of the added salt, then the calculations described may be reversed,

FIG. 2.

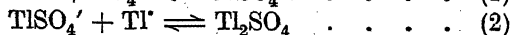
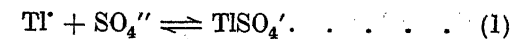


Activity coefficients of thallous chloride in the presence of: KCl, etc.  $\odot$ ; HCl  $\square$ ; BaCl<sub>2</sub>, etc.  $\oplus$ ; KNO<sub>3</sub>  $\diamond$ ; TlNO<sub>3</sub>  $\nabla$ ; Tl<sub>2</sub>SO<sub>4</sub>  $\triangle$ .

Broken curves are based on the assumption of complete dissociation. The full curve is based on an allowance for incomplete dissociation.

solubility measurements being made to provide a new method of determining the degree of dissociation of salts.

With the data already available the method can be applied to thallous sulphate, but here allowance must be made for the probable equilibria:



It seems reasonable to suppose, by analogy with sulphuric acid (Noyes and Sherrill, *J. Amer. Chem. Soc.*, 1926, 48, 1861), that in dilute solutions the amount of undissociated sulphate will be

negligibly small, and that step (2) may be disregarded as a first approximation. The dissociation constant of the first stage,  $K_1$ , can now be calculated from the solubility measurements in the following way. In 0.02*N*-thallous sulphate solution the solubility of thallous chloride is 0.01034 (Bray and Winninghoff, *loc. cit.*). If  $x$  is the concentration of  $\text{TlSO}_4'$ , the concentrations of the other species present are as follows:  $[\text{TlCl}] = 0.00068$ ;  $[\text{Cl}'] = 0.01034 - 0.00068 = 0.00966$ ;  $[\text{SO}_4''] = 0.01 - x$ ;  $[\text{Ti}'] = 0.00966 + 0.02 - x$ . The ionic strength of the solution is  $0.03966 - 2x$ , and we have  $f_{\pm}^2[\text{Ti}'][\text{Cl}'] = S$ , in which  $-\log f_{\pm} = 0.38\sqrt{\mu}$ . By successive approximations  $x$  can be found, and the left-hand side of the equation

$$\frac{[\text{Ti}'][\text{SO}_4'']}{[\text{TlSO}_4']} = \frac{K_1 \cdot f_{\text{TlSO}_4'}}{f_{\text{Ti}'} \cdot f_{\text{SO}_4''}} = K'_1$$

is thereby determined. The figures are shown in Table II, where the concentration of added salt and the solubility are in g.-equiv./l., and col. 4 gives  $K'_1$ , the "apparent dissociation constant" of the thallosulphate ion. Col. 5 shows the value of  $K_1$ , the true dissoci-

TABLE II.  
Added salt : Thallous sulphate.

Conc.	Solubility.	$\sqrt{\mu}$ .	$K'_1$ .	$K_1$ .
0	0.01612	0.1243	—	—
0.020	0.01034	0.1868	0.0876	0.0371
0.050	0.00626	0.2588	0.125	0.0380
0.100	0.00423	0.3463	0.169	0.0343

ation constant of this ion, calculated from  $K'_1$  on the assumptions that, at any ionic strength,  $f_{\text{TlSO}_4'} = f_{\text{Ti}'}$ , and  $f_{\text{SO}_4''}$  is given by the Debye-Hückel equation  $-\log f_{\text{SO}_4''} = 2.0\sqrt{\mu}$ : the values are as constant as could be expected in view of the probable errors of calculation and measurement; the mean value of  $K_1$  also agrees well with a second determination by a different method, which will be described in another paper. These figures are of interest as being the first obtained, on the basis of the interionic attraction theory, for the dissociation of a uni-bivalent salt, and they further emphasise the errors involved in a general application of the "complete dissociation of salts" hypothesis. Thus, the value  $K_1 = 0.036$  implies that in a 0.05*M*-solution of thallous sulphate about one-third of the total sulphate radical exists as  $\text{TlSO}_4'$ .

For thallous chlorate a single measurement is available; Noyes (*loc. cit.*) found the solubility of thallous chloride in 0.025*N*-thallous chlorate to be 0.00895 g.-equiv. per litre. Applying the same methods of calculation as before, we find the thallous chlorate to

be 6.4% undissociated, and give  $K = 0.34$  as a provisional value for the dissociation constant of this salt.

### *Summary.*

In determining activity coefficients by measuring the solubility of one salt in the presence of others, allowance must be made for the incomplete dissociation of the salts concerned. The necessary corrections are applied to the data for thalious chloride with the following results.

(1) The logarithm of the activity coefficient gives a straight line when plotted against the square root of the ionic strength up to a value of the latter considerably greater than 0.1.

(2) The slope of the curve is not 0.505, as the Debye-Hückel theory requires, but 0.38, a value previously found for several monobasic acids.

(3) The irregularities previously attributed to specific influences of the added ions disappear below a concentration of 0.1N, being due to neglect of incomplete dissociation of the salts.

(4) The dissociation constant of the  $\text{TiSO}_4^+$  ion is found to be 0.036, and that of thalious chlorate to be 0.34.

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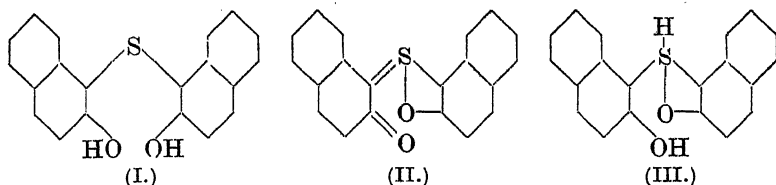
## CXVII.—*iso*- $\beta$ -Naphthol Sulphide.

By LEONARD ARTHUR WARREN and SAMUEL SMILES.

WHEN 2-naphthol 1-sulphide (I) is oxidised by alkaline ferricyanide, two hydrogen atoms are removed (J., 1914, 105, 1750) and the dehydro-sulphide is formed. Reduction of the latter substance yields the *iso*- $\beta$ -naphthol sulphide by absorption of two hydrogen atoms; these are removed by suitable oxidation, the dehydro-sulphide being regenerated (*loc. cit.*).

The *iso*-sulphide contains two active hydrogen atoms (J., 1913, 103, 346) and it yields lead and zinc derivatives which are insoluble in acetic acid (Hinsberg, *J. pr. Chem.*, 1914, 90, 345) in contrast with 2-naphthol 1-sulphide (I). Lesser and Gad (*Ber.*, 1923, 56, 970) found that a disulphide is formed from this *iso*-sulphide by oxidation with iodine and they obtained further evidence showing that the *iso*-sulphide is a hydroxy-mercaptan. These authors, assuming the structure (II) proposed by Hinsberg (*J. pr. Chem.*, 1915, 91, 307) for the dehydro-sulphide, considered that the *iso*- $\beta$ -naphthol sulphide should be represented by (III), which has the merit of providing a simple explanation of the conversion of the

substance into 2-naphthol 1-sulphide (I) by aqueous alkali hydroxide. On the other hand, this formula does not represent the substance



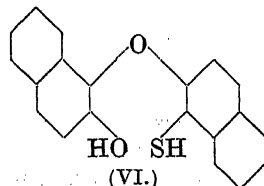
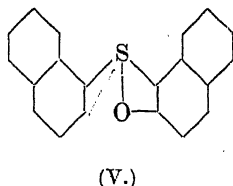
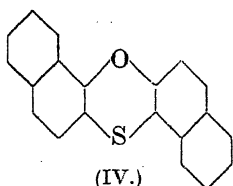
as a mercaptan, but assigns to it a dipolar structure derived from dinaphthylsulphonium hydroxide, to which the properties of a mercaptan can hardly be ascribed.

Apart from this criticism of a general nature, there are others which taken together make necessary a revision of the structure (III). For instance, the *iso*-sulphide is unattacked by aqueous acids and no indication of the formation of a sulphonium salt is obtained. If the dipolar structure and the explanation of the action of alkali which it affords were correct, acids as well as alkaline reagents should effect the conversion into 2-naphthol 1-sulphide (I). The zinc derivative of the *iso*-sulphide behaves as if the metal were associated with sulphur. With methyl iodide it gives a methyl ether (Hinsberg, *J. pr. Chem.*, 1916, **93**, 277) which is now shown to be the *S*-methyl derivative, since it is not oxidised by iodine and yields methyl mercaptan on reduction. This behaviour of the salt and its insolubility in acetic acid accord with the character of a zinc mercaptide. The *S*-methyl ether is not attacked by boiling aqueous alkali hydroxide or by boiling concentrated hydrochloric acid. According to the formula of Lesser and Gad (III with SMe in place of SH) 2-naphthol 1-sulphide should be obtained with these reagents, especially easily with the former, since Kehrman and Duttenhofer (*Ber.*, 1905, **38**, 4198) have shown that dinaphthyl-methylsulphonium decomposes rapidly under alkaline conditions, liberating the aromatic sulphide.

The *S*-methyl ether is converted by suitable oxidation into the sulphone: it is difficult to understand how a substance of that type could be formed from the structure in question (III; SH = SMe) without rupture of the molecule.

Finally,  $\alpha\beta\beta'\alpha'$ -dinaphthathioxin (IV) is obtained by dehydration of the *iso*-sulphide (J., 1913, **103**, 347, 909). Lesser and Gad, anticipating that this "*iso*"-dinaphthathioxin might have the structure later found to be correct (J., 1929, 210), assumed (*Ber.*, 1925, **58**, 2557) that migration of sulphur from the 1- to the 2-position takes place during dehydration and suggested a mechanism which involves the formation of a three-membered ring (V). This explan-

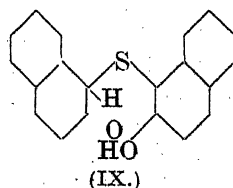
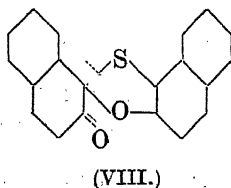
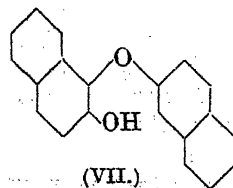
ation appears incomplete; moreover, there is difficulty in admitting that the dipolar structure would survive the attack of concentrated sulphuric acid while hydroxyl is being removed from the naphthalene nucleus. The experiments now described were undertaken as a result of these and other considerations.



Since it is evidently unsafe to attempt to derive any structure of the *iso*-sulphide from that hitherto ascribed to the dehydro-sulphide (II), the question has been approached independently. The chief characteristics of the *iso*-sulphide are those of a hydroxy-mercaptan (see, *e.g.*, Lesser and Gad, *loc. cit.*). When the substance is dehydrated,  $\alpha\beta\beta'\alpha'$ -dinaphthathioxin (IV) is formed: during the process, hydroxyl is removed and thiol survives as the thio-group. Interpreted in the simplest manner, this result leads to a structure such as (VI) for the *iso*-sulphide, which would thus appear as a derivative of 1:2'-dinaphthyl ether. Experiments have been made to isolate this group by removing sulphur from the substance.

Since the sulphonic group is easily removed from the naphthalene nucleus by alkaline reduction (Friedländer, *Ber.*, 1893, 26, 3208), the *S*-methyl ether was converted into the *sulphone*. This substance was easily attacked by sodium amalgam, the methanesulphonyl group being eliminated. The sulphur-free residue was identified as 2-hydroxy-1:2'-dinaphthyl ether (VII) by comparison of its *methyl* ether with the product synthesised from 1-bromo-2-methoxynaphthalene and potassium 2-naphthoxide in presence of copper.

Hydrogen iodide slowly attacked this sulphone, liberating methyl mercaptan, but with this reagent no pure substance was isolated from the sulphur-free products. On the other hand, the *S*-methyl ether, although slowly attacked by sodium amalgam under more

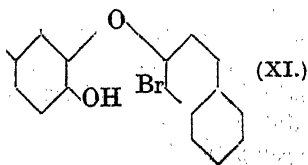
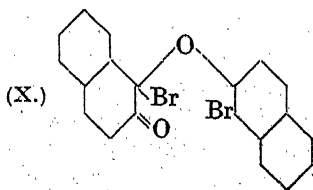


intense conditions, was easily attacked by hydrogen iodide, giving good yields of methyl mercaptan and the hydroxydinaphthyl ether

(VII) in question. Moreover, the *iso*-sulphide and the dehydro-sulphide were easily resolved by warm hydrogen iodide into hydrogen sulphide and this ether.

The *iso*-sulphide is therefore to be regarded as the thiol derivative of 2-hydroxy-1:2'-dinaphthyl ether, and, since  $\alpha\beta\beta'\alpha'$ -dinaphthathioxin (IV) is formed on dehydration, the thiol group must be in the 1'-position as indicated by (VI). This structure accords well with all the properties of the *iso*-sulphide hitherto observed and also with the formation of the sulphone and sulphonium derivatives now recorded.

With this information concerning the *iso*-sulphide, the constitution of the dehydro-sulphide may be profitably discussed. This substance is formed from 2-naphthol 1-sulphide (I) or the *iso*-sulphide (VI) by loss of two hydrogen atoms; evidently it contains the 1:1'-thio- and the 1:2'-oxido-group of the respective generators and should be represented as (VIII), reduction to the *iso*-sulphide taking place by rupture of the five-membered ring as indicated. The formation of the substance from 2-naphthol 1-sulphide may be represented as involving the oxidation of a tautomeric form of the latter (IX); some justification for this view (compare Willstätter and Schuler, *Ber.*, 1928, 61, 362) is found in the fact that this sulphide and others of its type yield only the monopotassium salts from solutions in more than two molecular proportions of the alkali hydroxide (Lesser and Gad, *Ber.*, 1925, 58, 2557). The structure (II) assigned by Hinsberg (*loc. cit.*) to this substance was founded on the formation of a monohydrazone and on experiments which indicated the formation of a very unstable perchlorate; but the existence of the latter substance cannot here be accepted as conclusively proving the presence of the sulphonium group, since it is well known that carbonyl in many ketones and quinones is capable of forming additive compounds with acids and salts (Pfeiffer, "Organisch Molekül-Verbindungen," 1927). The properties of the dehydro-sulphide are therefore adequately represented by the *spiro*-structure proposed. Moreover it should be noticed that this structure represents complete analogy with the dehydrophenols investigated by Pummerer (*Ber.*, 1914, 47, 1472, 2957; 1919, 52, 1392), who showed, for example, that dehydro-1-bromo-2-naphthol (X), which is obtained by oxid-



ation of 1-bromo-2-naphthol, yields on reduction the 1'-bromo-2-hydroxy-1:2'-dinaphthyl ether (XI), the quinolic bromine atom being eliminated. The greater stability of the dehydro-sulphide compared with that of other dehydrophenols is well explained by the presence of the five-membered thioxole system.

Finally it must be noticed that the conversion of the *iso*-sulphide into 2-naphthol 1-sulphide by heating or by the action of alkali hydroxide now appears to be an intramolecular change. Further experiments are being made concerning this process and the nature of dehydro-2-naphthol-1-sulphone.

#### EXPERIMENTAL.

The *iso*-2-naphthol sulphide (VI) used in these experiments was prepared as previously described (J., 1912, 101, 1423). The characteristic brown nickel derivative, formed by addition of nickel acetate to an alcoholic solution of the mercaptan, is very soluble in benzene.

*The S-Methyl Ether of the iso-Sulphide* (VI with SME in place of SH).—A concentrated solution of zinc acetate (10 g.) in hot water was added to a boiling solution of the *iso*-sulphide (20 g.) in alcohol (100 c.c.). The zinc salt (95%) separated in the crystalline state and was purer and more easily manipulated than the amorphous material prepared from cold solutions. A mixture of this zinc salt (10 g.), methyl iodide (5 c.c.), and ethyl alcohol (100 c.c.) was boiled until the zinc salt had dissolved (*ca.* 1 hour). The solvent was evaporated from the filtered solution and the residue was purified from acetic acid. The product (80–90%) had m. p. 134° (Found : C, 76.1; H, 4.8. Calc. : C, 75.9; H, 4.8%). The substance did not react with iodine in ethereal solution in presence of sodium bicarbonate, and it was recovered unchanged from a boiling ( $\frac{1}{4}$  hour) solution in aqueous sodium hydroxide (2*N*) and from a boiling (1½ hours) alcoholic solution containing hydrochloric acid. The formation of a yellow insoluble material when bromine vapour is added to an acetic acid solution may be conveniently used as a test for the presence of the substance.

The *benzoyl* derivative, prepared in cold pyridine, formed plates, m. p. 84–85° (Found : C, 77.2; H, 4.8.  $C_{23}H_{20}O_3S$  requires C, 77.1; H, 4.6%).

The *mercuri-iodide* of the *dimethylsulphonium iodide* (VI; SH =  $SMe_2I, HgI_2$ ) was rapidly formed when acetone containing equimolecular proportions of the *S*-methyl ether and mercuric iodide and a large excess of methyl iodide was boiled. After the mercuric iodide had dissolved, ether was added to the cooled liquid until it became turbid. The required substance separated in pale yellow



prisms, m. p.  $101^{\circ}$  (decomp.); these contained acetone which could not be quantitatively removed without further decomposition of the substance (Found: C, 32.1; H, 2.9; Hg, 20.0.  $C_{22}H_{19}O_2I_3SHg, 2C_3H_6O$  requires C, 32.1; H, 3.0; Hg, 19.2%).

The dimethyl ether of the *iso*-sulphide (VI; OH and SH = OMe and SMe respectively) was obtained as a clear viscous oil by the action of methyl sulphate on the sodium derivative of the *S*-methyl ether in methyl alcohol. It was characterised as the *methosulphate*, which was formed by heating a mixture of methyl sulphate ( $1\frac{1}{4}$  mols.) and the dimethyl ether (1 mol.) at  $100^{\circ}$  for 1 hour. The required substance was isolated from the product and further purified by addition of ether to a chloroform solution. It formed plates, m. p.  $178^{\circ}$  (decomp.), which were moderately easily soluble in water (Found: C, 61.4; H, 5.4; S, 13.3.  $C_{22}H_{18}O_2S, Me_2SO_4$  requires C, 61.0; H, 5.1; S, 13.6%).

The *S*-methylsulphone (VI; SH =  $SO_2Me$ ) was obtained by oxidation of the *S*-methyl ether. A product of this process has been described by Hinsberg (*J. pr. Chem.*, 1916, **93**, 277) as the sulphone derived from the monomethyl ether and as having m. p.  $218^{\circ}$ . The formation of a substance of this m. p. has been confirmed, but analytical data show that it is a mixture of sulphone and sulfoxide in approximately equal proportion (Found: C, 70.7; H, 4.7. Calc. for sulphone: C, 69.2; H, 4.4%. Calc. for sulfoxide: C, 72.4; H, 4.6%). Moreover, it was attacked by zinc and acetic acid, yielding a mixture of lower and indefinite m. p. ( $185$ – $190^{\circ}$ ) which was found by the bromine test to contain the *S*-methyl ether. The required sulphone was obtained by renewed oxidation. Acetic acid (20 c.c.) containing the *S*-methyl ether (4 g.) and hydrogen peroxide (8 c.c. of 30%) was heated at  $100^{\circ}$  for  $\frac{1}{2}$  hour and rapidly cooled. The product (4.1 g.), m. p.  $204$ – $209^{\circ}$ , was re-oxidised ( $\frac{1}{2}$  hour) with twice its weight of hydrogen peroxide (30%) in sufficient acetic acid for complete solution at  $100^{\circ}$ . The material (2.5 g.), which slowly separated from the cooled liquid, crystallised from acetic acid in plates, m. p.  $200^{\circ}$  (Found: C, 69.2; H, 4.5; *M*, 367.  $C_{21}H_{16}O_4S$  requires C, 69.2; H, 4.4%; *M*, 364). The substance was not attacked by zinc dust and acetic acid. The *benzoyl* derivative, prepared in cold pyridine, formed plates, m. p.  $149$ – $150^{\circ}$  (Found: C, 71.9; H, 4.7.  $C_{28}H_{20}O_5S$  requires C, 71.8; H, 4.3%). This substance was also obtained by oxidation of the *benzoyl* derivative of the *S*-methyl ether.

*2-Hydroxy-1:2'-dinaphthyl Ether* (VII).—This was obtained by the following methods: (a) A mixture of the *S*-methylsulphone (2 g.), aqueous sodium hydroxide (1 mol., 2*N*), ethyl alcohol (10 c.c.), and water (50 c.c.) was treated with sodium amalgam (150 g., 3%)

in the course of 12 hours, sufficient alcohol being added at intervals to redissolve insoluble material. Eventually the alcohol was evaporated and the sparingly soluble sodium salt was collected and decomposed with dilute sulphuric acid. The product (1 g.) crystallised from acetic acid in needles, m. p.  $197^{\circ}$ .

(b) The *S*-methyl ether (1 g.) was gently boiled with purified hydrogen iodide (25 c.c., *d* 1.7) in a long-necked flask. A slow stream of nitrogen passed through the apparatus, and the emergent vapours were washed by aqueous mercuric chloride. When the liberation of methyl mercaptan had ceased, the precipitated mercury derivative was collected (97%) (Found : Hg, 70.6. Calc. for  $\text{CH}_3\cdot\text{S}\cdot\text{HgCl}$  : Hg, 70.8%). The cooled contents of the reaction vessel were added to a large bulk of water; the solid was collected, washed (75%), and purified from acetic acid. It had m. p.  $197^{\circ}$ .

(c) A mixture of the zinc salt of the *iso*-sulphide (1 g.) and hydrogen iodide (10 c.c.) was treated as described in (b). Decomposition rapidly took place with liberation of hydrogen sulphide. The product, isolated and treated as described, was purified (36%) from acetic acid and had m. p.  $197^{\circ}$ .

(d) Similar treatment of the dehydro-sulphide (VIII) with hydrogen iodide gave hydrogen sulphide and a product which after purification (45%) had m. p.  $197^{\circ}$ .

The products from these four sources (*a*, *b*, *c*, and *d*) were identical with one another and with the product formed by reduction of dehydro-2-naphthol-1-sulphone (Hinsberg, *J. pr. Chem.*, 1915, 91, 307) under suitable conditions (Found : C, 84.0; H, 4.8. Calc. for  $\text{C}_{20}\text{H}_{14}\text{O}_2$  : C, 83.9; H, 4.9%). The structure suggested by Hinsberg (*Ber.*, 1915, 48, 2092) for this substance has been supported by Pummerer (*Ber.*, 1919, 52, 1414) and is now entirely confirmed by the synthesis of its methyl ether. It yielded a bromo-derivative, m. p.  $133$ – $134^{\circ}$ , apparently identical with that (XI) isolated by Pummerer and Cherbuliez (*loc. cit.*) from dehydro-1-bromo-2-naphthol; but no close comparison was made.

*2-Methoxy-1 : 2'-dinaphthyl Ether* (VII;  $\text{OH} = \text{OMe}$ ).—(a) Potassium 2-naphthoxide was prepared by heating (1 hour,  $110$ – $120^{\circ}$ ) the requisite quantities of 2-naphthol and potassium hydroxide in a current of nitrogen. A mixture of this material (2 mols.) and 1-bromo-2-methoxynaphthalene (1 mol.) containing a little copper acetate was heated (6 hours,  $230$ – $240^{\circ}$ ) in an atmosphere of nitrogen. During the process 2-naphthyl methyl ether sublimed; a further quantity of this substance was removed from the product by a current of steam in an alkaline medium. The dark-coloured insoluble material was set aside until it had solidified; then, when dry, it was heated in a vacuum (1–2 mm.). The desired *ether*

sublimed, and crystallised from acetone-alcohol in plates, m. p. 161°.

(b) The hydroxy-derivative (VII) obtained by the processes of reduction described above was methylated in aqueous alkaline solution with methyl sulphate. The product after purification had m. p. 161° and was identical with that obtained as described in (a) (Found : C, 83·7; H, 5·4.  $C_{21}H_{16}O_2$  requires C, 84·0; H, 5·3%).

In conclusion we wish to thank Dr. A. Cohen for the synthesis of 2-methoxy-1 : 2'-dinaphthyl ether and for his help in some of these experiments.

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### CXVIII.—*The Nitrosation of Phenols. Part VIII.* *Resorcinol Monoethyl Ether.*

By HERBERT HENRY HODGSON and HUBERT CLAY.

KIETAIBL (*Monatsh.*, 1898, **19**, 536) described two *o*-nitrosoresorcinol monoethyl ethers, but was unable to settle their constitutions. It has now been shown that in his nitrosation process 6-nitroso-3-ethoxyphenol alone is produced, for the product on oxidation gives only 6-nitro-3-ethoxyphenol : this compound has also been prepared from 4-nitro-3-aminophenetole, and both specimens give 4-nitro-resorcinol diethyl ether on ethylation.

Only the 3-chlorine could be replaced by ethoxyl when an excess of ethyl-alcoholic sodium ethoxide reacted with 1 : 3-dichloro-4-nitrobenzene (see Hodgson and Handley, J., 1928, 163, for the replacement of both chlorine atoms by methoxy-groups) : the 4-nitro-group renders the 3-carbon more positive than the 1-carbon atom by the general effect (Allan, Oxford, Robinson, and Smith, J., 1926, 401) and consequently the anionoid reagent ( $NaOAlk^{\oplus}$ ) first replaces the 3-chlorine by the  $OAlk$  group; but since ethoxyl is much more strongly anionoid than methoxyl, its excess of "negativity" so diminishes the general (electron-attracting) effect of the nitro-group on the 1-carbon atom that the anionoid reagent is unable under ordinary conditions to displace the chlorine atom in position 1.

The explanation of the predominant ortho-nitrosation of resorcinol monoethyl ether is similar to that for the monomethyl ether (Hodgson and Clay, J., 1929, 2775, formula I with Et in place of Me). With the assumption there made regarding the partly ionised hydroxyl group, since ethoxyl has a greater repressive effect on ionisation than methoxyl, the activation of hydrogen in the 4-position should be

relatively increased; moreover, the kationoid reagent in its polarised phase,  $\text{HONO}^{\oplus}$ , will have less tendency for attachment to the less highly charged phenolic hydroxyl group. On both counts the monoethyl ether should undergo nitrosation in the 4-position: this actually takes place to the extent of 10–15%. The same argument holds for nitration and is confirmed by the experimental results.

Alternatively, should the ethoxy-group exert an inductive electron-attraction, the 4-carbon (*loc. cit.*, formula III, with Et in place of Me) would be deactivated to a less extent in the ethoxy- than in the methoxy-compound, and so be relatively more reactive.

The solubility (1.32%) of 6-nitroso-3-ethoxyphenol in benzene is appreciably less than that (2.26%) of 6-nitroso-3-methoxyphenol, showing that the co-ordination (*loc. cit.*, formula V) of the *o*-nitroso- and the hydroxyl group is relatively weakened in the former compound. It would appear, therefore, that the increased repression of ionisation (see above) exceeds the concurrent increased activation of the chelating electrons of the nitroso-group.

#### EXPERIMENTAL.

*The Nitrosation of Resorcinol Monoethyl Ether.*—The method described by Hodgson and Clay (*loc. cit.*, p. 2777) for the nitrosation of resorcinol monomethyl ether, when applied to the monoethyl ether, gave a larger yield (5.5 g.) of crude product than that (4.7 g.) obtained by Kietaihl's method (*loc. cit.*). The quantities used were: resorcinol monoethyl ether 5 g., water 250 c.c., sodium hydroxide 2.5 g., sodium nitrite 3 g., concentrated sulphuric acid 5 c.c., water 100 c.c.

*Separation of the isomerides.* Kietaihl's method of extraction with boiling benzene was used, the operation being continued until the solvent remained practically colourless. From the extract, only one product could be crystallised, and this had the characteristics of Kietaihl's  $\alpha$ -*o*-nitroso-3-ethoxyphenol as described by Henrich (*J. pr. Chem.*, 1904, **70**, 313) (Found: N, 8.5. Calc.: N, 8.4%).

The residue insoluble in benzene (0.79 g.) crystallised from alcohol (charcoal) in small yellow needles, which slowly decomposed above 170° (Found: N, 8.6%).

*Oxidation of the Benzene-soluble Fraction with Dilute Nitric Acid.*—The substance (1 g.) was suspended in water (10 c.c.) and vigorously stirred during the gradual addition of 10 c.c. of a mixture of nitric acid (*d* 1.4; 3 parts) and water (1 part). After 5 hours, the mixture was diluted with water and the product was collected and distilled with steam; the 6-nitro-3-ethoxyphenol (0.9 g.) that passed over crystallised from alcohol or light petroleum in yellow needles, m. p.

and mixed m. p. with an authentic specimen (see later) 79° (Found : N, 7.8. Calc. : N, 7.65%). Weselsky and Benedikt (*Sitzungsber. Akad. Wiss. Wien*, 1880, **82**, 1219) describe a steam-volatile mononitro-derivative of resorcinol monoethyl ether as sulphur-gold needles, m. p. 79°.

*Oxidation of the Benzene-insoluble Fraction with Alkaline Potassium Ferricyanide.*—The substance (0.5 g.), dissolved in 10% aqueous potassium hydroxide (30 c.c.), was mixed with a saturated aqueous solution of potassium ferricyanide (10 g.) and heated on the water-bath until the colour became yellow. The solution was then filtered hot, cooled, and acidified. After some time, long greenish-yellow needles of 4-nitro-3-ethoxyphenol separated. These, after recrystallisation from dilute alcohol, melted, alone or mixed with an authentic specimen, at 131° (Found : N, 7.9. Calc. : N, 7.65%). The respective dibrominated products, separately or mixed, melted at 69° (Found : Br, 46.7, 47.0. Calc. : Br, 46.9%). Weselsky and Benedikt (*loc. cit.*) give m. p. 69° for 2 : 6-dibromo-4-nitro-3-ethoxyphenol.

*Oxidation of the Crude Nitrosation Mixture.*—(a) *With alkaline potassium ferricyanide.* The crude product (5 g.) was dissolved in 10% aqueous potassium hydroxide (300 c.c.) and oxidised with a saturated aqueous solution of potassium ferricyanide (100 g.) as described above. The solution was filtered hot, cooled, acidified with dilute sulphuric acid, and extracted with ether. The extracted product was steam-distilled : 6-nitro-3-ethoxyphenol (3.0 g.) passed over ; the liquor in the flask, on cooling, deposited a substance (1.5 g.) from which 4-nitro-3-ethoxyphenol (0.9 g.) was obtained by crystallisation from alcohol (charcoal). From the results of the oxidation of the benzene-soluble fraction (above), these combined amounts would account for almost the whole of the original crude mixture, to the exclusion of any other *o*-nitrosophenol such as Kietaihl's so-called  $\beta$ -*o*-nitroso-3-ethoxyphenol.

Under the above conditions the crude nitrosation product (3.0 g.) from resorcinol monomethyl ether yielded no 4-nitro-3-methoxyphenol, but gave 2.5 g. of the steam-volatile 6-nitro-isomeride.

(b) *With dilute nitric acid.* The crude nitrosation product (5 g.), suspended in water (60 c.c.), was oxidised as described above with 54 c.c. of dilute nitric acid. The yield of steam-volatile 6-nitro-3-ethoxyphenol was 3.6 g. The non-volatile residue consisted of tarry matter, from which a small amount of the 4-nitro-isomeride was obtained by extraction with ether.

*Nitration of Resorcinol Monoethyl Ether.*—The following method gives a better yield of the mononitro-derivatives than the method of Weselsky and Benedikt (*loc. cit.*). The ether (5 g.), dissolved in

acetic anhydride (20 c.c.), was nitrated below  $0^{\circ}$  by the gradual addition of nitric acid ( $d$  1.5; 2 c.c.) in acetic anhydride (8 c.c.). The mixture was kept over-night and then poured on ice. The precipitate was collected, washed, and steam-distilled; the volatile 6-nitro-3-ethoxyphenol (2.0 g.) crystallised from light petroleum in greenish-yellow needles, m. p.  $79^{\circ}$  (Weselsky and Benedikt, *loc. cit.*, give m. p.  $79^{\circ}$ ) (Found: N, 7.7. Calc.: N, 7.65%). The hot filtrate from the non-volatile tarry residue was cooled and extracted with ether, 0.5 g. of 4-nitro-3-ethoxyphenol being obtained which crystallised from alcohol in pale yellow needles, m. p.  $131^{\circ}$  (Weselsky and Benedikt, *loc. cit.*, give m. p.  $131^{\circ}$ ) (Found: N, 7.75. Calc.: N, 7.65%).

*Proof of the Constitution of 6-Nitro-3-ethoxyphenol.*—(a) *Conversion into 4-nitroresorcinol diethyl ether.* The potassium salt (1.3 g.), suspended in absolute alcohol, was heated under reflux with excess of ethyl iodide for 6 hours. The mixture was then made alkaline and steam-distilled; the volatile 4-nitroresorcinol diethyl ether (0.4 g.) crystallised from alcohol in almost colourless leaflets which, alone or mixed with an authentic specimen (Kauffmann and de Pay, *Ber.*, 1906, **39**, 2725), melted at  $85^{\circ}$  (Found: N, 6.9. Calc.: N, 6.6%). The liquor in the distillation flask, on acidification and steam-distillation, yielded 0.4 g. of unchanged 6-nitro-3-ethoxyphenol.

An attempt was made to obtain 4-nitroresorcinol diethyl ether by the action of excess of ethyl-alcoholic sodium ethoxide on 1:3-dichloro-4-nitrobenzene (compare Hodgson and Handley, *loc. cit.*). The product, however, was 3-chloro-6-nitrophenetole, which crystallised from alcohol in colourless leaflets, m. p.  $63^{\circ}$  (Blanksma, *Rec. trav. chim.*, 1904, **23**, 322, gives m. p.  $63^{\circ}$ ) (Found: Cl, 17.5. Calc.: Cl, 17.6%), identical with the product obtained from 3-chloro-6-nitrophenol by ethylation (compare Haworth and Lapworth, *J.*, 1923, **123**, 2986).

The same method, applied to 3-chloro-2-nitrophenol (13 g.), gave 3-chloro-2-nitrophenetole (12 g.), which crystallised from alcohol in colourless leaflets, m. p.  $52^{\circ}$  (Found: Cl, 17.5.  $C_8H_8O_3NCl$  requires Cl, 17.6%).

(b) *Synthesis from 3-chloro-4-nitrophenetole.* The ethylation of 3-chloro-4-nitrophenol as above gave 3-chloro-4-nitrophenetole, which crystallised from alcohol in colourless micro-prisms, m. p.  $39-40^{\circ}$  (Found: Cl, 17.4%). This was converted into 4-nitro-3-aminophenetole by heating it (2 g.) with concentrated aqueous ammonia (6 c.c.) and alcohol (5 c.c.) in a sealed tube at  $170-180^{\circ}$  for 8 hours. The product (1 g.), isolated from the reaction mixture after dilution with water, crystallised from alcohol in yellow needles,

m. p. 105–106° (Found : N, 15.5. Calc. : N, 15.4%), and was identical with a specimen prepared by the method of Reverdin and Lokietek (*Bull. Soc. chim.*, 1916, **19**, 252; *Arch. Sci. phys. nat.*, 1916, **42**, 47). The 4-nitro-3-aminophenetole (1 g.) was diazotised in dilute sulphuric acid and then converted by the standard procedure (Hodgson, E. P. 200714) into 6-nitro-3-ethoxyphenol (0.3 g.).

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### CXIX.—*The Nitrosation of Phenols. Part IX. Further Study of the Nitrosation of m-Bromophenol.*

By HERBERT HENRY HODGSON and ARNOLD KERSHAW.

THE alleged geometrical isomerides of 3-bromobenzoquinone-4-oxime (Hodgson and Moore, J., 1925, **127**, 2260) prove to have been impure specimens of one individual (compare 3-chlorobenzoquinone-4-oxime, J., 1929, 1553).

The chelation between the halogen and the oximino-hydrogen atom previously assumed (*loc. cit.*) in order to account for the stability of 3-chlorobenzoquinone-4-oxime appears to be even stronger in 3-bromoquinone-4-oxime, since this is much more stable to boiling dilute mineral acids than its 3-chloro-analogue : Auwers' cryoscopic data (*Z. physikal. Chem.*, 1903, **42**, 542) indicate that the co-ordination tendency of bromine is greater than that of chlorine.

3-Bromo-4-nitrosoanisole has an emerald-green colour, whereas 3-bromo-4-nitrosophenol is bright yellow, both in the solid state and in solution. 3-Bromobenzoquinone-4-oxime, however, gives pale green solutions, whereas its *methyl* ether is yellow and gives yellow solutions.

Similarly to the chloro-analogue, 3-bromo-4-nitrosophenol is converted immediately by concentrated sulphuric acid into the oxime; yet both substances give Liebermann nitrosoamine reactions, which differ in that the oxime produces a bluer colour.

The melting points of 3-bromo-4-nitrosoanisole (69°) and 3-bromobenzoquinone-4-oxime methyl ether (130°) are in accordance with the view expressed by Hodgson and Moore (*loc. cit.*), that nitroso-compounds melt at a lower temperature than the corresponding oximes.

## EXPERIMENTAL.

3-Bromobenzoquinone-4-oxime, prepared both by the alkali and by the acid method (*loc. cit.*), crystallises from benzene, in which it is sparingly soluble, in pale greenish-yellow, elongated parallelepipeds, m. p.  $196^{\circ}$  (compare Hodgson and Moore, *loc. cit.*) (Found : Br, 39.5; N, 7.0. Calc. : Br, 39.6; N, 6.9%).

The molecular weight of 3-bromo-4-nitrosophenol, determined cryoscopically, is 207 in naphthalene and 187 in phenol (calc., 202); the oxime is very sparingly soluble in naphthalene, but has  $M = 188$  in phenol. The benzoate, prepared and crystallised in the same way as the chloro-analogue, forms pale yellowish-brown, flat rhombs, m. p.  $181^{\circ}$  (Found : Br, 26.0.  $C_{13}H_8O_3NBr$  requires Br, 26.1%).

3-Bromo-4-nitrosoanisole (2.4 g.), prepared in the same way as the chloro-analogue (*loc. cit.*) by the oxidation of 3-bromo-4-aminoanisole hydrochloride (4.3 g.) with Caro's acid but with only 2 hours' stirring, crystallises from alcohol in emerald-green needles or prisms, m. p.  $69^{\circ}$  (Found : Br, 37.0.  $C_7H_6O_2NBr$  requires Br, 37.0%).

3-Bromobenzoquinone-4-oxime methyl ether is obtained by the addition of methyl sulphate to a solution of 3-bromobenzoquinone-4-oxime or 3-bromo-4-nitrosophenol in saturated aqueous sodium carbonate, followed by a few drops of aqueous sodium hydroxide. It is readily isolated by steam distillation and crystallises from 50% aqueous alcohol in yellow needles, m. p.  $130^{\circ}$  (Found : Br, 37.1.  $C_7H_6O_2NBr$  requires Br, 37.0%).

The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD. [Received, February 15th, 1930.]

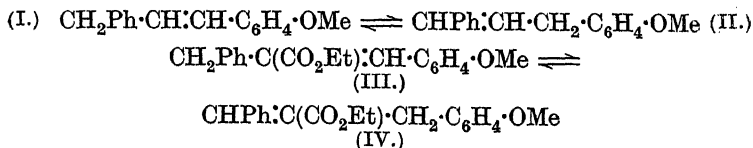
CXX.—Symmetrical Triad Prototropic Systems.  
Part VI. The Effect of Substitution on Tautomeric Mobility and Equilibrium in the  $\alpha$ -Diphenylpropene System.

By CHARLES WILLIAM SHOPPEE.

IN Part IV of this series (J., 1929, 447) tautomeric interchange between the isomerides (I  $\rightleftharpoons$  II) and (III  $\rightleftharpoons$  IV) was shown to occur in the presence of a catalyst, and methods were described whereby the mobility and equilibrium of such systems could be determined. The present paper gives an account of the systems



corresponding to (III  $\rightleftharpoons$  IV) for a series of *p*-substituents : Me, Cl, Br, I, NMe<sub>2</sub>, and  $\overset{\oplus}{\text{N}}\text{Me}_2\text{Et}$ .



Before the theoretical significance of the results is discussed, consideration must be given to certain fundamental principles underlying the relation of mobility and equilibrium to the structural features of a tautomeric system.

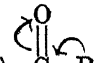
*Substitution and Mobility.*—In certain recent papers on prototropy and allied topics there has been a notable tendency to short-circuit the actual theory of the subject by referring to orientation in aromatic substitution as a practical criterion of the polar effects of groups and as, therefore, a direct analogy for their theoretically anticipated behaviour in relation to prototropic and other systems. Aromatic hydrogen-substitutions (even meta-) depend on the negativity of the field at the point of reaction, and the requisite electron availability may result either from the permanent *polarisation* of the molecule due to the electron repulsion (+ *I*) of a substituent, or from the molecular *polarisability* which is enhanced by the presence of a substituent containing unshared electrons, provided that a path exists for the propagation of electron displacements with covalency changes to the point of reaction (+ *T*) (compare Ingold and Shaw, J., 1927, 2923); these will be activating influences. Molecular polarisation resulting from a substituent possessing high electron-affinity (− *I*) will decrease electron-availability at the seat of reaction, and will be a deactivating influence, but polarisability arising from the presence of a substituent capable of sharing additional aromatic electrons and the existence of a free path for the electron transfer (− *T*) will not cause deactivation, because the displacements would lead to a recession of electrons from the seat of reaction, and for this there is no demand. On the other hand, prototropy depends on the positivity of the field at the seat of ionisation; the necessary electron-recession may arise from molecular polarisation due to the electron affinity (− *I*) of a substituent, or from molecular polarisability resulting from the presence of a substituent capable of sharing unshared electrons possessed by the system, provided that a path exists for the electron-transfer (− *T*); these will be facilitating influences. Molecular polarisation due to a substituent-repelling electron (+ *I*) will oppose the production of a positive field at the seat of ionisation, and hence will constitute

a retarding influence; molecular polarisability, resulting from the presence of a substituent possessing unshared electrons and capable of sharing these with the system if a path for the electron transfer exists (+  $T$ ), will not lead to electron displacements because such displacements would involve electron-accession to the seat of ionisation and for this there is no demand. In short, whereas

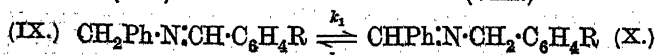
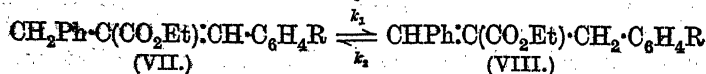
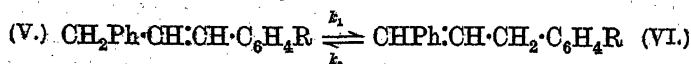
benzene hydrogen-	{	is facilitated by effects + $I$ and + $T$
substitution		is retarded by effect - $I$ only;
prototropy	{	is facilitated by effects - $I$ and - $T$
		is retarded by effect + $I$ only;

so that retardation of benzene hydrogen-substitution does not run parallel with facilitation of prototropy, and *vice versa*, unless *tautomeric effects of either sign* ( $\pm T$ ) are structurally impossible. Burton and Ingold exemplified this (J., 1928, 904) by stating that  $\text{NR}_3^+$  and COR activate prototropy by different mechanisms (-  $I$ , and -  $I - T$  respectively), but deactivate the benzene nucleus by the same mechanism (-  $I$  only; -  $T$  here being inoperative).

The +  $T$  effect can enter into the consideration of prototropy only when an activating group of the -  $I - T$  type is considered "piece-meal," and the +  $T$  effect of one portion is treated as subtractable from the (greater) -  $T$  effect of the other, as may be

possible, for instance, for COR in (three-carbon)  Since the order of +  $T$  effects of R is  $\text{O}^\ominus > \text{NR}_2 > \text{OR} > \text{Hals.} > \text{Me}$  (zero for the last member), that of the -  $T$  effect for COR is  $\text{COMe} > \text{COHal.} > \text{CO}_2\text{R} > \text{CO}\cdot\text{NR}_2 > \text{CO}\cdot\text{O}^\ominus$ , and this is the order of facilitation of prototropy (Ingold, Shoppee, and Thorpe, J., 1926, 1477). The -  $I$  effects of the same variants of the group COR are in the different order  $\text{COHal.} > \text{CO}_2\text{R} > \text{CO}\cdot\text{NR}_2 > \text{COMe} > \text{CO}\cdot\text{O}^\ominus$  (Cooper and Ingold, J., 1927, 838), and this is all that enters into the theory of aromatic substitution (-  $T$  is inoperative), and is the order of *m*-orientation. This point has been treated at some length because of Linstead's recent comments (J., 1929, 2498) on the apparent lack of agreement between the two series.

In continuation of previous investigations (J., 1929, 447, 1199), in which it was shown that systems of the forms



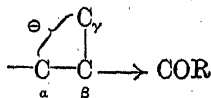
became mobile in the presence of sodium ethoxide, it has now been proved for the system (VII  $\rightleftharpoons$  VIII)—system (IX  $\rightleftharpoons$  X) is still being investigated—that the effect of R on the velocity of inter-conversion under constant conditions of temperature and catalysis is as follows (time units, hours)\* :

Group R	NMe <sub>2</sub> .	OMe.	I.	Br.	Cl.
$k_1 + k_2$ .....	<<0.050	0.058	0.39	0.64	1.02
Moment .....	+1.39	-0.80	-1.25	-1.51	-1.56

The bottom row of the table contains the recorded values of the molecular electric moments of the compounds C<sub>6</sub>H<sub>5</sub>R in E.S.U.  $\times 10^{-18}$ , the attached sign indicating the polarity of R; the numbers are direct measures of the state of polarisation ( $\pm I$ ) induced by R directly attached to the aromatic nucleus in a series of compounds such as those investigated. The parallelism between this measure of  $-I$  and the mobility figures will be obvious.

None of the groups investigated is known to exert a  $-T$  effect; if it had been capable of so doing, the parallelism would, of course, have failed (*e.g.*, COR, CN, NO<sub>2</sub>). On the other hand, the groups tabulated are all structurally capable of  $+T$  effects, but this, as already explained, does not enter into prototropy (when the *whole* activating group is considered and not merely a part of it). The cases, therefore, differ from those studied by Kon and Linstead, which involve the  $-T$  effect, and an alternative statement of the difference is that the systems examined by these investigators are pentad keto-enols, involving the common enolide ion  $\text{C}=\text{C}-\text{C}=\text{C}-\overset{\text{O}}{\underset{\text{S}}{\text{O}}}$ .

Although the three-carbon systems here examined contain a group (carbethoxyl) normally capable of a  $-T$  effect, the position of this ( $\beta$ -) is such that this effect cannot be propagated by tautomeric electron displacements to the seat of ionisation. A feeble  $-I$  effect should, however, reach the ionising centre, and in addition to this, polar and steric disturbances due to the spatial proximity of the group are to be anticipated.

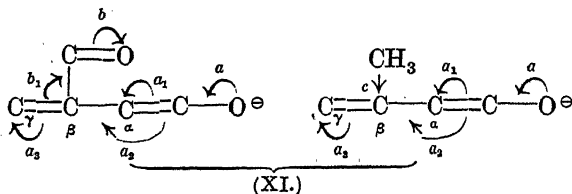


In this connexion, Linstead's argument (*loc. cit.*) that the preliminary ionic dissociation is unimolecular, whereas the final recombination of ions is bimolecular, and that this furnishes a basis for consideration of the mechanism of steric inhibition in prototropy,

\* The value for R = Me is of the same order as for R = OMe, but is not tabulated because the velocity coefficients were not good enough to give an accurate significance to their mean. Theoretically, Me should fit in between OMe and NMe<sub>2</sub>.

is unacceptable to the writer, who regards the catalyst as promoting ionic dissociation; from this point of view the dissociation must at least be bimolecular, for it is common knowledge that it depends on the catalyst (*e.g.*,  $\text{OEt}^\ominus$  ion) as well as on the compound ionised.

*Substitution and Equilibrium.*—The general theory of the effect of substitution on equilibrium in three-carbon systems containing activating groups of the  $-I-T$  type (pentad keto-enol and pentad cyano-imino systems) has already been given (Ingold, Shoppee, and Thorpe, *loc. cit.*; Ingold, *Ann. Reports*, 1927, 111; 1928, 118; Bennett, *ibid.*, 1929, 119), and is in excellent agreement with the available data, including the most recent results (Kon and Linstead, J., 1929, 1269; Kandiah and Linstead, *ibid.*, p. 2139); nevertheless, confusion has again arisen, through the application of the process previously described as short-circuiting. Ingold, Shoppee, and Thorpe discussed the effect of a  $\beta$ -carbethoxyl group and showed that it should lead ( $-T$  effect) to predominance of the  $\beta\gamma$ -unsaturated form (*e.g.*, in the system citraconic ester-itaconic ester, the latter is the favoured phase). Linstead has concluded from this (*loc. cit.*) that the theory implies that a  $\beta$ -methyl group ( $+I$  effect) should produce the opposite result, that is, a stable  $\alpha\beta$ -form, which is contrary to fact (Goldberg and Linstead, J., 1928, 2343). It cannot be too strongly insisted that the effect of  $+I$  cannot be deduced by mechanical inversion of that of  $-T$ , and that all such short cuts involve unsound procedure, with the sole exceptions of that for  $+I$  to  $-I$ , and its converse. In the case considered, the formulæ (XI) show the enolide ions in the critical

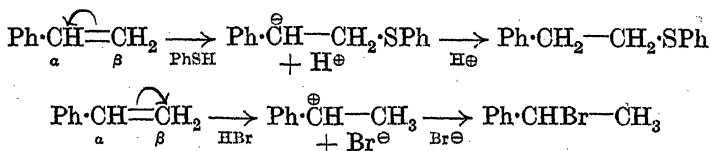


stage immediately preceding their combination with a proton. The  $-T$  effect of the  $\beta$ -carbethoxyl group ( $b, b_1$ ) acts on the displaceable double-bond electrons, inhibiting  $a_3$ ; the  $+I$  effect of the  $\beta$ -methyl group ( $c$ ) acts on the  $\beta$ -carbon atom, charging it negatively and directing the electrons away from  $a_2$  into the alternative route  $a_1$ ; since  $a_3$  depends on initiation from  $a_2$  (which in turn depends on  $a$ ), the  $+I$  effect ( $c$ ) will also, indirectly, inhibit  $a_3$ . The facts (that the influences of  $\beta$ -methyl and  $\beta$ -carbethoxyl groups are qualitatively similar) are thus in complete agreement with the theory.

Reference is also necessary to another point raised by Linstead, namely, the effect of  $\beta$ - and  $\gamma$ -phenyl substituents. The polar effect

of the phenyl group is represented by  $\pm T$ , that is, it is able to furnish either electron-accession to or electron-recession from an adjacent carbon atom, according to the sign of the field required at the seat of reaction. This duplex polar capacity of the phenyl group is manifested in its ability to activate both prototropy (these papers) and anionotropy (Burton and Ingold, *loc. cit.*), and to confer stability on free radicals (*idem*, *Proc. Leeds Phil. Soc.*, 1929, i, 421). Owing to its ambi-polar charge-distributing mechanism, phenyl

tends to absorb the charge on  $C_a$  in either polarisation  $\text{Ph}-\overset{\curvearrowright}{\text{C}}_a=\text{C}_\beta$ ,  $\text{Ph}-\text{C}_a=\overset{\curvearrowleft}{\text{C}}_\beta$ , with the result, *inter alia*, that  $\text{Aryl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2[\text{H}]$  and  $\text{Aryl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2[\text{Br}]$  are stable tautomerides; to attribute such phenomena to a special "non-polar element of stability associated with conjugated systems" is to conceal their essentially polar nature. Probably the simplest illustration of the duplex polar functions of phenyl is that additions of either polar sign to styrene are uniformly initiated at  $C_\beta$  (Ingold, *Ann. Reports*, 1928, 146); for instance, addition of thiophenol to styrene occurs through the strongly basic (prone to co-ordinate) potential anion  $\text{PhS}^\ominus$ , whereas in the addition of hydrogen bromide the relatively unstable potential kation (proton) commences the attack; addition is probably initiated by a partly polarised molecule, with subsequent liberation of the more stable ion of the additive complex :



Now in the case of a  $\gamma$ -phenyl substituent, consideration of formula (XII), which shows the enolide ion in the critical stage preceding co-ordination of the proton, indicates that charge absorption will deactivate  $C_\gamma$  (like  $C_a$  in styrene) and the proton will combine at  $C_a$ ;



the phenyl group could activate  $C_\beta$  towards a proton (like  $C_\beta$  in styrene), but the structure is such that  $C_\beta$  cannot take advantage of this tendency. In the case of a  $\beta$ -phenyl substituent (XIII), the phenyl group will activate  $C_\gamma$  towards a proton (like  $C_\beta$  in styrene) and this will favour combination at  $C_\gamma$ ; the other effect, namely, deactivation of  $C_\beta$  (like  $C_a$  in styrene), does not enter into the problem for obvious reasons. Once again it is seen that the theory is adequate when properly applied.

In the experimental work here described, special attention has been given to the establishment of a small, but apparently real, anomaly, for which several explanations, none of which can as yet be proved, are possible. The system examined is the simple three-carbon system formulated on p. 970 ( $\text{VII} \rightleftharpoons \text{VIII}$ ), and the substituents R are of the forms normally characterised by the effects  $-I$ ,  $-I + T$ , and  $+I$ . In the simple three-carbon system the anionic charge is necessarily borne by carbon and the essential consideration determining equilibrium pertains to the relative ionisability of the isomerides. Obviously the predominance of form (VII) (see equation) should diminish as the electron-affinity of R decreases (from  $-I$  to  $+I$ ). The table shows that, although the three kinds of groups are arranged in the right way, the members of the central group are inverted amongst themselves.

Type	$-I$		$-I + T$		$+I$
R	NMe <sub>2</sub> Et	OMe	Br	Cl	Me
VII (%)	>90	56.5	54.0	50.0	48.0

It is thought that this anomaly is probably related to the similar anomalies revealed in Tasman's results on the alkaline hydrolysis of phthalides (*Rec. trav. chim.*, 1927, **46**, 653) and in Kindler's on the alkaline saponification of benzoic esters (*Annalen*, 1926, **450**, 1), though in the latter two examples of aromatic side-chain reactivity the anomaly relates to the halogens only and does not include methoxyl. It is possible (but the point must await proof) that these apparent inversions are dependent on changes shown to be possible by Sidgwick's limiting-valency rule, and in a classification of groups relating to an aspect of aromatic substitution more closely analogous to prototropy than ordinary hydrogen substitution, a  $-T$  effect has tentatively been ascribed to halogens (other than fluorine) in the presence of basic reagents.

## EXPERIMENTAL.

### Methyl Compounds.

$\alpha$ -*p*-Methylbenzylcinnamic Acid (formula as VIII).—*p*-Methylcinnamic acid was obtained in 70% yield by condensing *p*-tolu-aldehyde with malonic acid in pyridine solution in the presence of piperidine on the steam-bath.  $\beta$ -*p*-Tolylpropionic acid can be obtained from it by reduction with phosphorus and hydriodic acid (von Miller and Rohde, *Ber.*, 1890, **23**, 1898), but is contaminated with a considerable quantity of *p*-toluic acid: the use of 3% sodium amalgam (Krober, *ibid.*, p. 1053) gives a pure product.

Sodium  $\beta$ -*p*-tolylpropionate (45 g.), benzaldehyde (26 g.), and acetic anhydride (30 g.) were heated together at 160° for 10 hours,

the melt was poured into a solution of crystallised sodium carbonate (150 g.) and extracted with ether, and the extract washed twice with 2*N*-sodium hydroxide. The ethereal extract contained a hydrocarbon, and the alkaline washings on acidification yielded 2 g. of  $\alpha$ -*p*-methylbenzylcinnamic acid, which separated from dilute alcohol in long prisms, m. p. 181°, and instantly decolorised alkaline permanganate (as did also all the substituted cinnamic acids described later in this paper) (Found: C, 81.0; H, 6.4.  $C_{17}H_{16}O_2$  requires C, 80.9; H, 6.3%). A further quantity was obtained from the sodium carbonate solution by acidification and fractional crystallisation of the product from dilute alcohol.

$\alpha$ -Benzyl-*p*-methylcinnamic Acid (formula as VII).—*p*-Tolualdehyde (48 g.), sodium  $\beta$ -phenylpropionate (69 g.), and acetic anhydride (49 g.) were heated at 150° for 8 hours and the procedure described above (sodium carbonate, 300 g.) was then followed. The sodium hydroxide washings on acidification yielded  $\alpha$ -benzyl-*p*-methylcinnamic acid (2 g.), which separated from alcohol in needles, m. p. 200° (Found: C, 80.8; H, 6.3%). A further quantity (5 g.) was isolated from the sodium carbonate solution. The ethereal extract yielded 25.5 g. of *p*-tolualdehyde, b. p. 92–94°/13 mm., and a hydrocarbon.

The following m. p.'s are uncorrected, but were determined under identical conditions. The m. p.'s of artificial mixtures of the two preceding acids lie on a two-branch curve, the eutectic point of which corresponds to a mixture, m. p. 163°, containing 64.0% of  $\alpha$ -*p*-methylbenzylcinnamic acid (A).

A, %	0.0	20.8	35.2	47.9	56.8	68.2	85.1	100.0
M. p.	200.0°	190.0°	181.5°	175.5°	168.0°	165.0°	173.5°	181.0°

*Interconversion of the Ethyl Esters.*—*Preparation of the esters.* These two esters, and those described subsequently, were obtained by the action of ethyl iodide upon the silver salts. Ethyl  $\alpha$ -*p*-methylbenzylcinnamate (VIII; R = Me) is a colourless oil, b. p. 178–180°/1 mm., 197–198°/6 mm. (Found: C, 81.2; H, 7.2.  $C_{19}H_{20}O_2$  requires C, 81.4; H, 7.2%). Ethyl  $\alpha$ -benzyl-*p*-methylcinnamate (VII; R = Me) also is a colourless oil, b. p. 205–207°/7 mm.,  $n_D^{20}$  1.58415 (Found: C, 81.0; H, 7.4%).

*Alkaline hydrolysis of the esters.* The standard conditions and the method of isolation described for the methoxy-compounds (J., 1929, 447) were employed. As only a small quantity (0.01 g.) was used for a m. p. determination, the whole of the hydrolysis product was first melted, to ensure homogeneity. The ester (VII) gave 96% of unpurified acid, m. p. 200.0°, and the ester (VIII) gave 95%, m. p. 180.5° (the m. p.'s of the pure acids are 200.0° and 181.0°, respectively).

These results establish (a) that no interconversion of the isomerides takes place in the presence of hydroxide ions at 100° under the conditions given, and (b) that, since the yields are practically quantitative in both cases, and no impurities affecting the m. p.'s of the acids are introduced, hydrolysis and subsequent thermal analysis of the acids can be used to follow the interconversion of the esters.

*Stability of the esters to heat.* Redistillation of the esters and subsequent hydrolysis gave the same results. The esters were interconverted under the standard conditions (1.45*N*-alcoholic sodium ethoxide at 85°), the approach towards equilibrium being followed by hydrolysis under the standard conditions, and thermal analysis.

Isomeride used.	Time at 85° with NaOEt (hours).	M. p. of acids.	Isomeride VIII, %.	$k_1 + k_2$ (hour <sup>-1</sup> ).
VII	0.0	200.0°	0.0	—
	4.0	191.5	17.0	0.099
	10.5	179.0	39.0	0.132
	22.0	172.5	50.5	0.059
	31.0	172.0	51.0	0.065
	48.0	171.5	52.0	—
	68.0	171.5	52.0	—
VIII	48.0	171.5	52.0	—
	22.0	162.0	64.0	0.063
	2.0	176.0	89.0	0.115
	0.0	181.0	100.0	—

Equilibrium : VIII (52.0%)  $\rightleftharpoons$  (48.0%) VII;  $k_1 + k_2$  (mean) = 0.088 hr.<sup>-1</sup>;  $k_1/k_2 = 1.083$ ;  $k_1 = 0.0046$ ;  $k_2 = 0.0042$ .

#### *Chloro-compounds.*

*$\alpha$ -p-Chlorobenzylcinnamic Acid* (formula as VIII).—*p*-Chlorocinnamic acid was obtained by condensing *p*-chlorobenzaldehyde (50 g.) and malonic acid (37 g.) with piperidine (5 c.c.) in pyridine (125 c.c.); it separated from alcohol in fine colourless needles (yield, 85%), m. p. 244–245°. Gabriel and Herzberg (*Ber.*, 1883, 16, 2037) described it as yellow and indistinctly crystalline, m. p. 240–242°. The acid was rapidly reduced by 3% sodium amalgam at about 45° and gave a 75% yield of  $\beta$ -*p*-chlorophenylpropionic acid, m. p. 122° after crystallisation from dilute acetic acid.

Sodium  $\beta$ -*p*-chlorophenylpropionate (62 g.), benzaldehyde (32 g.), and acetic anhydride (34 g.) were heated at 160° for 8 hours and the melt was poured into a solution of 100 g. of crystallised sodium carbonate. After 12 hours, the white solid was filtered off, washed with ether, suspended in warm water, and agitated with hydrochloric



acid. The precipitate was filtered off and twice crystallised from alcohol,  $\alpha$ -*p*-chlorobenzylcinnamic acid being obtained in clusters of prisms (10 g.), m. p. 194.5° (Found: C, 70.0; H, 4.9.  $C_{16}H_{13}O_2Cl$  requires C, 70.4; H, 4.8%).

Extraction of the aqueous liquor with ether gave a solution containing a chlorohydrocarbon and the above acid (4 g., removed by sodium hydroxide); on acidification, the sodium carbonate solution gave a further quantity of the acid (57 g., crude).

*p*-Chloro- $\alpha$ -benzylcinnamic Acid (formula as VII).—Sodium  $\beta$ -phenylpropionate (49 g.), *p*-chlorobenzaldehyde (40 g.), and acetic anhydride (35 g.) were heated together for 8 hours at 160°, and the melt was poured into a solution of 100 g. of crystallised sodium carbonate. The solution was extracted with ether and then acidified. The acid product separated from boiling alcohol in colourless needles, m. p. 163°, unchanged by further crystallisation (Found: C, 68.5, 68.6; H, 4.5%). These figures indicate that the product consisted of a mixture of the required acid (82%) and *p*-chlorocinnamic acid (18%); these could not be separated by fractional crystallisation. The mixed acids (10 g.) were treated with two successive quantities of sodium carbonate (50 c.c.; 2.2 g.  $Na_2CO_3$  in 150 c.c. water), from which, by acidification of the two filtrates, three fractions, A, B, and C, were obtained.

Fraction A, recrystallised from alcohol, melted at 223–225° and consisted largely of *p*-chlorocinnamic acid.

Fractions B and C, recrystallised from alcohol, gave *p*-chloro- $\alpha$ -benzylcinnamic acid in colourless needles, m. p. 171.5° (Found: C, 70.3; H, 4.7%).

Mixtures of  $\alpha$ -*p*-chlorobenzylcinnamic and *p*-chloro- $\alpha$ -benzylcinnamic acids melted as follows: A denotes the former acid.

A, %	0	20.6	31.6	36.2	42.0	45.9	50.3	53.6	69.7	100.0
M. p.	171.5°	162.5°	156.5°	153.5°	155.0°	161.0°	165.0°	168.0°	178.0°	194.5°

*Interconversion of the Ethyl Esters.*—Ethyl  $\alpha$ -*p*-chlorobenzylcinnamate (VIII; R = Cl) has b. p. 197°/3 mm. and separates from ligroin (b. p. 40–60°) in prisms, m. p. 55° (Found: C, 71.8; H, 5.8.  $C_{18}H_{17}O_2Cl$  requires C, 71.9; H, 5.7%). Ethyl *p*-chloro- $\alpha$ -benzylcinnamate (VII; R = Cl) has b. p. 208°/6 mm. (Found: C, 71.8; H, 5.7%).

Under standard conditions, hydrolysis of (VIII) afforded a quantitative yield of the corresponding acid, m. p. (crude) 194°, and (VII) gave a 99% yield of its acid, m. p. 170.5°.

The interconversion of the esters in 1.45*N*-alcoholic sodium ethoxide was observed in the manner described for the methoxy- and methyl compounds.

Isomeride used.	Time at 85° with NaOEt (hours).	M. p. of acids.	Isomeride VIII, %.	$k_1 + k_2$ (hours <sup>-1</sup> ).
VII	0	171.5°	0	—
	1.0	148.0*	41.0	(1.71)
	2.0	157.5	43.5	1.02
	16.0	165.0	50.0	—
	32.0	165.0	50.0	—
VIII	16.0	165.0	50.0	—
	8.0	165.0	50.0	—
	2.0	169.5	56.0	1.07
	1.0	176.5	67.0	1.08
	0.5	185.0	82.0	0.90
	0	194.5	100.0	—

\* This is very near the eutectic.

Equilibrium : VIII (50.0%)  $\rightleftharpoons$  VII (50.0%);  $k_1 + k_2$  (mean) = 1.02 hr.<sup>-1</sup>;  $k_1/k_2 = 1.00$ ;  $k_1 = k_2 = 0.51$ .

### Bromo-compounds.

*α-p-Bromobenzylcinnamic Acid* (formula as VIII).—Sodium *β-p*-bromophenylpropionate (Gabriel and Zimmermann, *Ber.*, 1880, **13**, 1683) (67 g.), benzaldehyde (28 g.), and acetic anhydride (33 g.) were heated together for 10 hours at 160° and the melt was submitted to the usual treatment. The sodium hydroxide washings of the ethereal extract yielded on acidification *α-p-bromobenzylcinnamic acid*, which crystallised from alcohol in prisms, m. p. 200° (Found : C, 60.8; H, 4.1. C<sub>16</sub>H<sub>13</sub>O<sub>2</sub>Br requires C, 60.5; H, 4.1%). The sodium carbonate liquor gave a large quantity of an acid, which was not investigated, and the ethereal extract contained a bromohydrocarbon.

*p-Bromo-α-benzylcinnamic Acid* (formula as VII).—*p*-Bromobenzaldehyde (Jackson and White, *Ber.*, 1878, **11**, 1023) (24 g.), sodium *β*-phenylpropionate (23 g.), and acetic anhydride (17 g.) were similarly treated. The sodium hydroxide washings gave *p-bromo-α-benzylcinnamic acid*, which was obtained in fine long needles, m. p. 193°, after several crystallisations from ethyl acetate-ligroin (Found : C, 60.5; H, 4.0%). The sodium carbonate solution yielded a large quantity of *p-bromocinnamic acid*, m. p. 257° after two crystallisations from boiling absolute alcohol (Found : C, 47.8; H, 3.0. Calc. for C<sub>9</sub>H<sub>7</sub>O<sub>2</sub>Br : C, 47.6; H, 3.1%). The ethereal extract contained a bromohydrocarbon.

Mixtures of the two acids melted as follows : A denotes *α-p*-bromobenzylcinnamic acid :

A, %	0	15.9	35.1	57.2	68.0	86.2	100.0
M. p.	193.0°	186.0°	177.0°	178.0°	184.0°	192.5°	200.0°

*Interconversion of the Ethyl Esters*.—Ethyl *α-p*-bromobenzylcinnamate (VIII; R = Br) is a colourless oil, b. p. 200°/1 mm.

(Found : C, 62.6; H, 4.9.  $C_{18}H_{17}O_2Br$  requires C, 62.6; H, 4.9%). Hydrolysis under the standard conditions affords the corresponding acid, m. p.  $200^\circ$  without purification, in 98% yield. *Ethyl p-bromo- $\alpha$ -benzylcinnamate* (VII; R = Br) is a colourless oil, b. p.  $200^\circ/3$  mm. (Found : C, 62.6; H, 5.0%); on hydrolysis under the standard conditions it gives the corresponding acid, m. p.  $193^\circ$  without purification, in 98.5% yield.

The esters were interconverted under the standard conditions and the process was followed by hydrolysis (standard conditions) and thermal analysis. In the case marked with an asterisk 0.45 g. of ester was used.

Isomeride used.	Time at $85^\circ$ with NaOEt (hours).	M. p. of acids.	Isomeride VIII, %.	$k_1 + k_2$ (hour $^{-1}$ ).
VII	0	193.0°	0	—
	2.0	178.0	33.0	0.631
	24.0	172.0	46.0	—
	36.0	172.0	46.0	—
	24.0	172.0	46.0	—
VIII	12.0	171.5	46.5	(0.375)
	4.8	172.5	48.0	0.671
	2.0	181.0	62.5	0.592
	1.0*	185.5	71.0	0.659
	0	200.0	100.0	—

Equilibrium : VIII (46.0%)  $\rightleftharpoons$  VII (54.0%);  $k_1 + k_2$  (mean) = 0.64 hr. $^{-1}$ ;  $k_1/k_2 = 0.852$ ;  $k_1 = 0.30$ ;  $k_2 = 0.34$ .

#### *Iodo-compounds.*

*$\alpha$ -p-Iodobenzylcinnamic Acid* (formula as VIII).—*p*-Iodobenzaldehyde was prepared by oxidation of *p*-iodobenzyl bromide with copper nitrate solution and had m. p.  $76^\circ$ . The aldehyde (20 g.) and malonic acid (9 g.) were condensed in pyridine solution with piperidine (2 c.c.); the *p*-iodocinnamic acid obtained separated from boiling alcohol in colourless prismatic needles, m. p.  $264^\circ$  (decomp.) (Gabriel and Herzberg, *Ber.*, 1883, 16, 2039, describe the acid as yellow and incompletely crystalline, decomposing at  $255^\circ$  without melting) (Found : C, 39.4; H, 2.6. Calc. for  $C_9H_7O_2I$ : C, 39.4; H, 2.6%).

Gabriel and Herzberg obtained the dihydro-acid by reduction with phosphorus and hydriodic acid for a short period (undefined). Little reduction takes place under these conditions, and the use of sodium amalgam in alkaline solution at  $45^\circ$  yields only  $\beta$ -phenylpropionic acid.  $\beta$ -*p*-Iodophenylpropionic acid is best obtained by iodination of  $\beta$ -phenylpropionic acid in 50% acetic acid with a 10% excess of iodine monochloride. The mixture, which becomes hot, is kept on the steam-bath for  $\frac{1}{2}$  hour. After 12 hours, the product is dissolved in ether and the solution is washed with aqueous sodium

thiosulphate and with water, dried, and evaporated. A large part of the residual oil solidifies after 48 hours; the acid is drained and then crystallised from 40% acetic acid; m. p. 139°. Yield, 14 g. from 50 g. of  $\beta$ -phenylpropionic acid.

Sodium  $\beta$ -*p*-iodophenylpropionate (34.5 g.), benzaldehyde (12.5 g.), and acetic anhydride (13 g.) were heated at 150–155° for 6 hours and the melt was poured into a solution of sodium carbonate (50 g.). After 12 hours, the solid (sodium salt of the required acid) was removed and washed with ether; the filtrate was extracted with ether. The extract, after being washed with *N*-sodium hydroxide, contained an iodohydrocarbon. The sodium carbonate solution, acidified with 2*N*-hydrochloric acid at 0°, gave  $\alpha$ -*p*-iodobenzylcinnamic acid (5 g.), m. p. 219.5° after crystallisation from glacial acetic acid (Found: C, 52.5; H, 3.5.  $C_{16}H_{13}O_2I$  requires C, 52.7; H, 3.6%). The sodium hydroxide washings also gave a small quantity of this acid.

*p*-Iodo- $\alpha$ -benzylcinnamic Acid (formula as VII).—*p*-Iodobenzaldehyde (46 g.), sodium  $\beta$ -phenylpropionate (34 g.), and acetic anhydride (25 g.) were heated together at 170–180° for 7 hours; the melt was poured into excess of sodium carbonate solution and treated as in the preceding case. The ethereal extract and the sodium hydroxide washings contained an iodohydrocarbon and  $\beta$ -phenylpropionic acid respectively.

The solid initially precipitated by the sodium carbonate was suspended in 2*N*-hydrochloric acid at 40–45° and stirred for  $\frac{1}{2}$  hour; the product was a mixture of *p*-iodocinnamic acid (2 parts) and *p*-iodo- $\alpha$ -benzylcinnamic acid (1 part), which could not be separated by fractional crystallisation (Found: C, 44.7, 44.8; H, 3.0, 3.1%). The mixture (10 g.) was converted through the acid chlorides (by thionyl chloride) into the ethyl esters, which were distilled. The lower fraction obtained (5 g.), b. p. 175–180°/5 mm., mainly at 177°/5 mm., crystallised readily, and separated from ice-cold ligroin (b. p. 40–60°) in long needles, m. p. 37–37.5°, consisting of ethyl *p*-iodocinnamate, identical with a specimen prepared from synthetic *p*-iodocinnamic acid. The second fraction (3.5 g.), b. p. 180–230°/5 mm., partly solidified; after being drained, the solid was crystallised from ligroin (b. p. 40–60°), giving ethyl *p*-iodo- $\alpha$ -benzylcinnamate, m. p. 53.5° (Found: C, 54.9; H, 4.4.  $C_{18}H_{17}O_2I$  requires C, 55.1; H, 4.4%). On hydrolysis under the standard conditions, this ester gave pure *p*-iodo- $\alpha$ -benzylcinnamic acid, m. p. 232° after crystallisation from alcohol (Found: C, 52.3; H, 3.7%).

On account of the decomposition which occurred in the later stages of the foregoing distillation, the following separation is to be preferred. The mixed acids (25 g.) were treated with a solution of

2.2 g. of sodium carbonate at 100° and the hot liquid was filtered. The filtrate gave a granular precipitate (A) on acidification. Repetition of the process afforded a flocculent precipitate (B). Recrystallisation of (A) and (B) from alcohol gave *p*-iodocinnamic acid (13 g.) and *p*-iodo- $\alpha$ -benzylcinnamic acid (7 g.), m. p. 229–230°, respectively. The sodium hydroxide washings (above) also gave a very small quantity of the latter acid.

Mixtures of  $\alpha$ -*p*-iodobenzylcinnamic acid (C) and *p*-iodo- $\alpha$ -benzylcinnamic acid melted as follows :

C, %	0	19.0	39.0	47.2	57.0	61.0	66.4	79.1	100.0
M. p.	232.0°	222.0°	210.5°	206.5°	201.5°	199.0°	204.0°	210.0°	219.5°

*Interconversion of the Ethyl Esters.*—Ethyl  $\alpha$ -*p*-iodobenzylcinnamate (VIII; R = I) has b. p. 212–214°/2 mm., and melts at 46.5° after crystallisation from ligroin (b. p. 40–60°) (Found : C, 55.0; H, 4.4. C<sub>18</sub>H<sub>17</sub>O<sub>2</sub>I requires C, 55.1; H, 4.4%). Ethyl *p*-iodo- $\alpha$ -benzylcinnamate (VII; R = I), m. p. 53.5°, prepared from the silver salt was identical with the ester described above.

*Hydrolysis.* The esters (VII) and (VIII) gave quantitative yields of the respective acids, m. p.'s 232° and 219°, on hydrolysis with aqueous-alcoholic alkali (standard conditions). They are hydrolysed with extraordinary ease by acids, even by cold 2*N*-acetic acid.

*Action of sodium ethoxide.* Treatment of either ester with 1.45*N*-sodium ethoxide at 85° caused conversion into the other, since, by hydrolysis under the standard conditions and fractional crystallisation of the product from acetic acid, both acids were obtained. Owing to the presence of impurities produced by a secondary reaction, probably involving the iodine atom, the composition of the equilibrium mixture of the acids could not be determined from the melting-point diagram. The esters could not be distilled owing to hydrolysis taking place, and the following procedure was therefore adopted.

Preliminary experiments indicated that the ester (VII) was more prone to decomposition than the isomeride (VIII); and that the quantity of the new isomeride produced during very short periods of interconversion ( $\frac{1}{4}$ — $\frac{1}{2}$  hour) was insufficient to give, after hydrolysis, a saturated solution of the corresponding acid in ethyl acetate at 0°. To minimise errors due to the secondary reaction, the ester (VIII) was employed : it was treated with 1.45*N*-sodium ethoxide at 85°, the product hydrolysed under the standard conditions, and the acids isolated in the usual manner. A known weight (0.20 g.) of the cooled fused acids was dissolved in ethyl acetate, and the solution concentrated by evaporation in a graduated test-tube as far as was

possible without separation of solid. The solution, its volume having been noted, was kept for 16 hours in the ice-chest and the crystalline product was then collected and weighed. Its composition was determined by thermal analysis (the mixtures showing binary character), and a correction made for the solubility of each isomeride in a saturated ethyl acetate solution of the other at 0°.

Time at 85° with NaOEt (hrs.).	Wt. crude acids (g.).	Wt. cryst. acids (g.).	Vol. EtAc (c.c.).
2	0.1990	0.1428	1.7
3	0.1994	0.1425	2.0
4	0.1998	0.1522	2.0
M. p. of cryst. acids.	% Isomeride VII.	% VII, corr. for solubility.	$k_1 + k_2$ (hr. <sup>-1</sup> ).
203.0*	35.0	33.7	0.47
200.0*	38.5	36.8	0.37
200.5†	42.0	40.2	0.33

\* Depressed by trace of acid (VII).

† Elevated by trace of acid (VII).

Owing to the secondary reaction, the equilibrium point could not be ascertained. The velocity coefficients are calculated on the basis of the assumed equilibrium  $\text{VIII (45\%)} \rightleftharpoons \text{(55\% VII)}$ , which is approximately that found for the bromo-esters.

The solubility of  $\alpha$ -*p*-iodobenzylcinnamic acid (0.00592 g./c.c.) and of *p*-iodo- $\alpha$ -benzylcinnamic acid (0.00157 g./c.c.) in a saturated ethyl acetate solution of the other was determined by saturating ethyl acetate with both acids, keeping the solution at 0° for 16 hours, and evaporating a known volume of the solvent; the composition of the residue was found by thermal analysis.

#### *Dimethylamino-compounds.*

$\alpha$ -*p*-Dimethylaminobenzylcinnamic Acid (formula as VIII).—*p*-Dimethylaminobenzaldehyde (300 g.) and malonic acid (213 g.) were heated in pyridine (500 c.c.) in the presence of piperidine (20 c.c.) for some hours on the steam-bath. When the mixture ceased to evolve carbon dioxide, it was poured into a large volume of ice-water containing 500 c.c. of glacial acetic acid. The precipitate crystallised from boiling alcohol in yellow plates (335 g.), m. p. 225° (vig. decomp.). Weil (*Monatsh.*, 1908, 29, 899) gives m. p. 216° (decomp.).

The foregoing acid (250 g.) was reduced with 3% sodium amalgam at 45–50°, and the product isolated by acidification with hydrochloric acid (Congo) and treatment with saturated sodium acetate solution. The  $\beta$ -*p*-dimethylaminophenylpropionic acid formed colourless prisms, m. p. 106°, from dilute alcohol: a further quantity was obtained by extraction of the mother-liquor with ether (total yield, 140 g.). The sodium salt (120 g.), benzaldehyde (60 g.), and

acetic anhydride (66 g.) were heated together for 9 hours while the temperature rose from 160° to 180°, the melt was then poured into an excess of sodium carbonate solution, and the mixture was extracted with ether after standing. The aqueous liquid, by acidification and treatment with sodium acetate solution with mechanical stirring, afforded  $\alpha$ -*p*-dimethylaminobenzylcinnamic acid (24 g.), m. p. 146° after repeated crystallisation from methyl alcohol (Found: C, 76.7; H, 6.7.  $C_{18}H_{19}O_2N$  requires C, 76.9; H, 6.8%). A little more was obtained by acidification of the sodium hydroxide washings of the ethereal extract; the latter contained a small quantity of the *p*-dimethylamino-base.

*p*-Dimethylamino- $\alpha$ -benzylcinnamic Acid (as VII).—Condensation of potassium  $\beta$ -phenylpropionate (63 g.), *p*-dimethylaminobenzaldehyde (50 g.), and acetic anhydride (38 g.) at 160–170° for 9 hours, and isolation of that portion of the product soluble in hydrochloric acid but precipitated by sodium acetate, furnished an acid, m. p. 232° (decomp.) after crystallisation from methyl alcohol. The quantity was insufficient for analysis, but the following observations indicate that the acid was *p*-dimethylamino- $\alpha$ -benzylcinnamic acid.

$\alpha$ -*p*-Dimethylaminobenzylcinnamic acid was heated with sodium ethoxide solution under the standard conditions for 48 hours; the product was isolated by acidification and addition of sodium acetate. Crystallisation from methyl alcohol yielded  $\alpha$ -*p*-dimethylamino-benzylcinnamic acid, m. p. 144°, and a less soluble acid, m. p. 230° (decomp.) after repeated crystallisation (m. p. of a mixture with the above acid, 229° decomp.). Ozonolysis in glacial acetic acid solution yielded an acid, m. p. above 200° (*p*-dimethylaminobenzoic acid?), in quantity insufficient for complete purification; benzoic acid was not obtained.

$\alpha$ -*p*-Dimethylaminobenzyl- and *p*-dimethylamino- $\alpha$ -benzylcinnamic acids do not yield a m. p.—composition diagram of the usual form, probably owing to decomposition of the latter acid. Since thermal analysis could not be employed to estimate the composition of mixtures of the acids, the ethyl esters were investigated. Ethyl  $\alpha$ -*p*-dimethylaminobenzylcinnamate (VIII;  $R = NMe_2$ ) was obtained from the silver salt of the corresponding acid by treatment with 1 mol. of ethyl iodide in an equal volume of chloroform; it separated from ligroin (b. p. 40–60°) in rectangular prisms, m. p. 62.5° (Found: C, 77.6; H, 7.4.  $C_{20}H_{23}O_2N$  requires C, 77.6; H, 7.5%). On hydrolysis under the standard conditions it gave the corresponding acid, m. p. 146° without purification. As partial hydrolysis during isolation of the mixed esters obtained by equilibration of this ester with 1.45*N*-sodium ethoxide could not be prevented, the

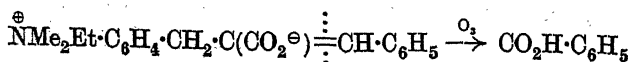
preparation of the isomeric ester (VII) and the plotting of a m. p.-composition diagram for the esters were not proceeded with.

The conversion of the ester (VIII) into its isomeride in the presence of 1.45*N*-sodium ethoxide could be proved qualitatively only after 65 hours' treatment: from 0.50 g. of the ester (VIII), 0.02 g. of *p*-dimethylamino- $\alpha$ -benzylcinnamic acid, m. p. 229—230°, was isolated after hydrolysis under the standard conditions; the remainder (0.38 g.) consisted of the more soluble isomeric acid. These experiments indicate a minimum conversion of about 4% in 65 hours; in the absence of knowledge relating to the position of equilibrium, and assuming this to be of the same order as that found for the methoxy-compounds (J., 1928, 447), it appears that the mobility of the dimethylamino-compounds is much smaller than that of the methoxy-compounds.

#### *Dimethylethylammonium Compounds.*

*Internal Salt of p- $\beta$ -Carboxy- $\gamma$ -phenylallylphenyldimethylethylammonium Hydroxide.*—Silver  $\alpha$ -*p*-dimethylaminobenzylcinnamate was treated with an excess of ethyl iodide on the steam-bath for  $\frac{1}{2}$  hour. The mixture of crystalline solid and silver iodide produced was extracted with much boiling acetone. The extract, on addition of ligroin, cooling, and stirring, gave the *molecular compound* of *p*- $\beta$ -carbethoxy- $\gamma$ -phenylallylphenyldimethylethylammonium iodide and silver iodide (1 mol.) in colourless pearly plates, m. p. 155—156° (Found: C, 38.4; H, 4.0; ionic I, 18.5, 18.6; AgI, 34.3.  $C_{22}H_{28}O_2NI \cdot AgI$  requires C, 37.8; H, 4.0; ionic I, 18.1; AgI, 33.6%). By treatment with silver hydroxide in warm aqueous acetone solution, filtration, evaporation, and addition of alcoholic picric acid, *p*- $\beta$ -carbethoxy- $\gamma$ -phenylallylphenyldimethylethylammonium *picrate*, m. p. 130° after crystallisation from methyl alcohol, was obtained (Found: C, 58.6; H, 5.2.  $C_{28}H_{30}O_9N_4$  requires C, 59.3; H, 5.3%).

The molecular compound was boiled in aqueous-acetone solution with silver chloride, and the filtered solution evaporated; prolonged desiccation yielded a resinous solid, which could not be purified. This was probably the betaine, since it contained no ionisable halogen and gave with sodium picrate a sodium salt-picrate, m. p. 270° (decomp.). A satisfactory analysis could not be obtained, but ozonolysis in glacial acetic acid solution gave an almost quantitative yield of benzoic acid:





The resinous solid (0.50 g.) was treated with a solution of 0.54 g. of sodium in 15 c.c. of ethyl alcohol (giving an active ethoxide-ion concentration equal to that of 1.45*N*-sodium ethoxide) for 24 hours at 85°. The cooled product was poured into water, neutralised with hydrochloric acid, and evaporated to dryness. The residue was extracted with successive small quantities of hot glacial acetic acid and the combined extracts were treated with ozonised oxygen. From the ether-soluble portion of the decomposition products, only a trace of benzoic acid (a few mg.) could be isolated. The water-soluble portion yielded no identifiable substance.

Attempts were made to synthesise the pairs of isomerides in which the *p*-substituents were NHAc or CN. *p*-Cyanobenzaldehyde, m. p. 100°, prepared from *p*-cyanobenzyl bromide, condensed with sodium β-phenylpropionate and acetic anhydride at 160° to yield almost entirely *p*-cyanocinnamic acid, m. p. 254° after crystallisation from nitrobenzene (Found: C, 68.5; H, 3.6. Calc. for C<sub>10</sub>H<sub>7</sub>O<sub>2</sub>N: C, 69.4; H, 4.0%). *p*-Acetamidobenzaldehyde, sodium β-phenylpropionate, and acetic anhydride at 180–200° gave an *acid*, m. p. 267° after repeated crystallisation from nitrobenzene, to which no formula has been assigned (Found: C, 71.2, 71.3; H, 5.5, 5.8; N, 5.7, 5.7%). *p*-Acetamidocinnamic acid, yellow prismatic needles, m. p. 261° (decomp.), was readily obtained in 78% yield from *p*-acetamidobenzaldehyde and malonic acid in the presence of piperidine. Reduction of this with sodium amalgam at 40–45° in the presence of carbon dioxide afforded β-*p*-acetamidophenylpropionic acid, which crystallised from 2*N*-acetic acid as the *monohydrate*, m. p. 124° after softening at 87–88° (Found: C, 59.3; H, 6.6. C<sub>11</sub>H<sub>13</sub>O<sub>3</sub>N.H<sub>2</sub>O requires C, 58.8; H, 6.7%). Desiccation gave the anhydrous acid, m. p. 143°. Sodium β-*p*-acetylphenylpropionate, benzaldehyde, and acetic anhydride condensed at 160–170° to furnish an *acid*, m. p. 233–234°, of unknown constitution (Found: C, 71.0; H, 5.8; N, 4.9, 4.9%).

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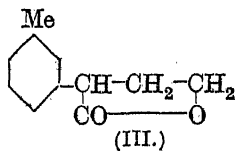
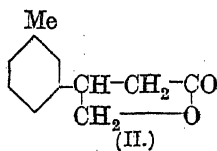
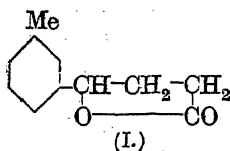
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# CXXI.—Cannabis Indica Resin. Part I. The Constitution of Nitrocannabinolactone (Oxycannabin).

By ROBERT SIDNEY CAHN.

THE general problem presented by *Cannabis Indica* resin, the essential portion of the drug known as hashish, bhang, etc., will be considered in a later communication. The present paper is confined to oxycannabin, which is a product of oxidation by concentrated nitric acid of the higher-boiling portions of the resin.

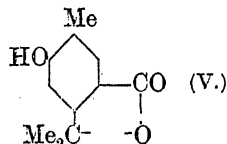
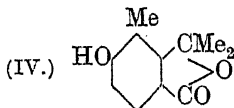
Oxycannabin has been assigned various formulæ, viz.,  $C_{20}H_{20}O_7N_2$  (Bolas and Francis, J., 1869, **22**, 417; *Chem. News*, 1871, **24**, 77),  $C_{10}H_{11}O_4N$  (Dunstan and Henry, P., 1898, 44), and  $C_{11}H_{11}O_4N$  (Wood, Spivey, and Easterfield, J., 1899, **75**, 20), the last of which has been confirmed in the present investigation. Wood, Spivey, and Easterfield removed the nitro-group, *via* the amino- and iodo-groups, to obtain the substance  $C_{11}H_{12}O_2$ ; this they termed cannabinolactone, renaming oxycannabin as nitrocannabinolactone. Among other results they showed that cannabinolactone on fusion with potassium hydroxide yielded *m*-toluic acid, and as, further, it contains an excessively stable lactone group, they concluded that it must be represented by one of the  $\gamma$ -lactonic formulæ (I)—(III).



They did not, however, consider the possibility of its being a phthalide derivative, although these are known readily to yield derivatives of benzoic acid on fusion with alkali.

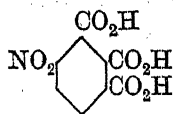
*Hydroxycannabinolactone* was chosen as the starting point of the present investigation, as it was hoped by means of this substance to determine also the position of the substituent group (compare Bauer, *Ber.*, 1908, **41**, 503, who obtained *m*-hydroxybenzoic acid from methoxy- $\alpha\alpha'$ -diethylphthalide). Hydroxycannabinolactone (prepared by boiling a diazotised solution of the amino-compound) on fusion with potassium hydroxide at 290–300° yielded 6-hydroxy-*m*-toluic acid and acetone, which are the products to be expected from a substance having either formula (IV) or (V) (Gucci, *R. Accad. Lincei*, 1897, **6**, i, 295). The production of acetone renders untenable formulæ (II) and (III) for cannabinolactone (also those representing it as an ethylphthalide), but is not incompatible with

formula (I). In this last case oxidation, starting at the carbon atom carrying the hydroxyl group formed by opening of the lactone

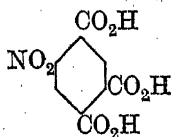


ring, would yield potassium malonate, from which acetone would be formed. Wood, Spivey, and Easterfield, however, showed that only the methyl group of cannabinolactone was oxidised by excess of alkaline potassium permanganate solution, and the present author found that under similar conditions nitrocannabinolactone absorbs only the three atoms of oxygen necessary for oxidation of the methyl group. On account of the stability of the alcoholic hydroxyl group, which must be present in alkaline solutions of cannabinolactone and its nitro-compound, it is impossible to regard these substances as primary or secondary alcohols.\* The only constitution which gives rise to a tertiary alcoholic group on ring opening is that of a dimethylphthalide, for which the two possibilities (IV) and (V) remain.

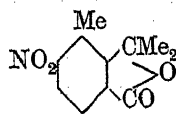
A by-product in the nitric acid oxidation of nitrocannabinolactone was a tribasic acid,  $C_9H_5O_8N$ , m. p. 228—230°, the formation of which Wood, Easterfield, and Spivey were unable satisfactorily to explain on the basis of their formulæ (I)—(III). However, the dimethylphthalide formulation being assumed, this acid clearly has the structure represented by (VI) or (VII). The former has not



(VI.)



(VII.)



(VIII.)

been synthesised. The latter melts at 175° (Schultz, *Ber.*, 1909, 42, 3607) and thus cannot be identical with the acid from nitrocannabinolactone, which must, therefore, be (VI). Nitrocannabinolactone itself must then be represented by formula (VIII).

During the preliminary experiments on the alkali fusion of hydroxycannabinolactone it was found that there was considerable danger of loss of carbon dioxide from the hydroxy-acid formed. In order to determine the conditions of the reaction, 4-hydroxy-dimethylphthalide (IX) was prepared from the corresponding amino-

\* *E.g.*, mandelic acid was found to be readily oxidised under the conditions used for nitrocannabinolactone.

compound\* (Teppema, *Rec. trav. chim.*, 1923, **42**, 30; Tasman, *ibid.*, 1927, **46**, 653). The cannabinolactone derivatives behave very similarly to those encountered in this preparation, the methylation of the hydroxy-derivative being particularly noteworthy, and the relative stability of the nitro-, amino-, and methoxy-compounds agrees qualitatively with that established by Tasman (*loc. cit.*) for phthalide derivatives. In an attempt to effect fission by a



method in which the possibility of oxidation was excluded, 4-hydroxydimethylphthalide was heated with aniline to 300°. A nearly quantitative yield of 4-hydroxy-N-phenyl- $\alpha$ -dimethylphthalimidine (X) resulted: the same compound was also obtained by heating with aniline and aniline hydrochloride to 210° (compare Emmert and Meyer, *Ber.*, 1921, **54**, 210).

#### EXPERIMENTAL.

Nitrocannabinolactone (oxycannabin), prepared according to the directions of Wood, Spivey, and Easterfield (*loc. cit.*), had the properties described by these authors (Found †: C, 59.8, 59.6; H, 5.1, 5.0; N, 6.6, 6.55; *M*, in camphor, 206, 196, 203, 212. Calc. for  $C_{11}H_{11}O_4N$ : C, 60.0; H, 5.0; N, 6.35%; *M*, 221). The working up of the hashish used for this preparation will be described in a later communication.

*Aminocannabinolactone*.—The following modification of Wood, Spivey, and Easterfield's method of preparation is more convenient and gives an improved yield. Red phosphorus (5 g.) was added to a solution of nitrocannabinolactone (9 g.) in glacial acetic acid (36 c.c.) and hydriodic acid (27 c.c., *d* 1.7), and the whole heated under reflux for 2–3 hours. The solution was diluted with water (300 c.c.) and filtered hot into a hot solution of sodium hydroxide (34 g.) in water (500 c.c.). The weakly acid solution was again filtered hot from a small amount of gummy impurity, which was washed with boiling water. On cooling, aminocannabinolactone (5.3 g.) separated as an oil which at once crystallised when seeded and was quite pure, m. p. 120° (Wood, Spivey, and Easterfield give m. p. 119°). By concentration of the mother-liquor (charcoal) a further quantity (0.5 g.) was obtained, m. p. 117–118° (total yield, 74.5% of the theoretical).

\* Named 5-aminodimethylphthalide by these authors, who start numbering from the carbonyl group.

† All analyses marked thus are microanalyses by Dr. Ing. A. Schoeller of Berlin.

*Hydroxycannabinolactone* (IV).—When potassium nitrite (2.54 g. in a little water) was added to a cold solution of aminocannabinolactone (5.7 g.) in 20% sulphuric acid (110 c.c.), and the mixture subsequently warmed on the water-bath until evolution of gas ceased, *hydroxycannabinolactone* separated in quantitative yield as an apricot-coloured powder. Recrystallised from aqueous alcohol or, better, from benzene, it formed pale yellow needles, m. p. 198—199° (Found †: C, 68.5; H, 6.3.  $C_{11}H_{12}O_3$  requires C, 68.7; H, 6.3%). The colour cannot be removed by ordinary methods, but the substance was recovered quite colourless from low-temperature potash fusions. *Hydroxycannabinolactone* dissolves immediately in cold sodium hydroxide and slowly in sodium bicarbonate solutions (to give bright yellow solutions, if the coloured substance is used), and is precipitated unchanged on acidification. An alcoholic solution does not, however, evolve carbon dioxide on treatment with sodium bicarbonate solution. Acetylation by acetic anhydride was not satisfactory, but *acetoxycannabinolactone* was readily obtained by addition of acetyl chloride to an ice-cold solution of the substance in pyridine and subsequent treatment with water. It crystallised from a little alcohol in colourless needles, m. p. 93° (Found †: C, 66.3; H, 6.1.  $C_{13}H_{14}O_4$  requires C, 66.6; H, 6.0%).

*Methoxycannabinolactone*.—On shaking a solution of hydroxycannabinolactone (0.9 g.) in 8% sodium hydroxide solution with methyl sulphate (20 c.c., added in portions), a homogeneous solution was obtained, from which *methoxycannabinolactone* was precipitated on acidification. It crystallised from methyl alcohol in colourless prisms, m. p. 182° [Found †: C, 69.6; H, 6.9; MeO, 14.1.  $C_{11}H_{11}O_2(OMe)$  requires C, 69.9; H, 6.8; MeO, 15.05%].

Once precipitated, the methoxy-compound is insoluble in sodium hydroxide solution, and the phthalide ring is only slowly opened; e.g., after the methoxy-compound (0.3 g.) had been refluxed with 10% aqueous-alcoholic potassium hydroxide solution (1:1) for 1 hour, addition of water precipitated 0.1 g. which had not undergone ring fission, the remainder being precipitated on acidification (compare Tasman, *loc. cit.*). As the methoxy-compound, when first formed, remained dissolved in the alkaline solution, it must have been formed as  $OH \cdot CMe_2 \cdot C_6H_2Me(OMe) \cdot CO \cdot O-$ . Whence it follows that the dimethylphthalide ring of the hydroxy-compound is opened on solution in cold alkali, and that the doubts of Tasman, who did not investigate hydroxy-compounds, as to the quinonoid structure of phenolphthalein compounds are unfounded.

*Methoxycannabinolactone* was also obtained by heating the hydroxy-compound in benzene solution with methyl iodide and

freshly prepared silver oxide, and by heating the silver salt with methyl iodide in benzene.

*Fusion of Hydroxycannabinolactone.*—The lactone (1 g.) was added during 8 minutes to molten potassium hydroxide at 290—300°, this temperature being maintained for a further 10 minutes. The cooled melt was dissolved in water, acidified, and then made alkaline with sodium bicarbonate. Extraction with ether removed a small amount of cresol and unchanged phthalide. Re-acidification of the alkaline liquid and extraction with ether yielded impure 6-hydroxy-*m*-toluic acid, which after recrystallisation from water formed needles containing  $\frac{1}{2}\text{H}_2\text{O}$  of crystallisation (Found:  $\text{H}_2\text{O}$ , 5.95, 6.4. Calc. for  $\text{C}_8\text{H}_8\text{O}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ :  $\text{H}_2\text{O}$ , 5.6%). When dried, it melted at 172—173° (Found: C, 63.45; H, 5.25. Calc. for  $\text{C}_8\text{H}_8\text{O}_3$ : C, 63.15; H, 5.3%). Yield after one crystallisation, 0.3 g. The acid gave no colour with ferric chloride solution.

The distillate from a similar fusion was collected under water and gave positive results with the following tests for acetone: iodoform, sodium nitroprusside-alkali-acetic acid, Denigès's test.

*Oxidation of Nitrocannabinolactone.*—4% Potassium permanganate solution was added in portions of 1 c.c. to a solution of nitrocannabinolactone (0.47 g.) and sodium hydroxide (1 g.) in water (15 c.c.) heated on the water-bath. Decolorisation, at first complete in 15 seconds, grew progressively slower until, when 16.4 c.c. (3 atoms of oxygen) had been added, 20 minutes were required. Thereafter, decolorisation was exceedingly slow, and on addition of a further 5.5 c.c. (1 atom of oxygen) and continued heating for 1 hour, very little reduction took place. After cooling, excess of sodium bisulphite and hydrochloric acid were added, which precipitated a rapidly crystallising gum. Recrystallised from water, it formed plates (0.2 g.), m. p. 227—229° (Wood, Spivey, and Easterfield give the melting point of cannabinolactonic acid as 229—230°).

4-*Hydroxy- $\alpha\alpha$ -dimethylphthalide* (IX).—4-Aminodimethylphthalide (Teppema, *loc. cit.*; Tasman, *loc. cit.*) was prepared (*a*) by the method described above for aminocannabinolactone, the pure compound crystallising (m. p. 117°) in 78% yield, or (*b*) by suitable modification of West's method (J., 1925, 127, 494), in 70% yield. For transformation into the hydroxy-compound the following conditions should be adhered to, deviations leading to much reduced yields. 4-Aminodimethylphthalide (8.85 g.) in water (100 c.c.) and concentrated sulphuric acid (10 c.c.) was diazotised at 10° by potassium nitrite (4.25 g. in a little water), and the cooled solution dropped slowly into boiling, mechanically stirred 1% sulphuric acid (500 c.c.). Boiling and stirring were continued for a further 2 hours and the solution was then filtered hot from a little tar. On standing

in the ice-chest, 4-hydroxy- $\alpha$ -dimethylphthalide (6.9 g.; 78% of the theoretical yield) was deposited in pale yellow crystals. It separated from benzene in very pale yellow crystals, m. p. 149–150° (Found: C, 67.5; H, 5.8.  $C_{10}H_{10}O_3$  requires C, 67.4; H, 5.7%). The substance was purified beyond this point only with difficulty, but was recovered from low-temperature potash fusions quite colourless and melting at 152°.

The acetyl derivative was prepared by the pyridine and acetyl chloride method, and crystallised from dilute acetic acid; it melted at 84°.

When the hydroxy-compound (0.5 g.), dissolved in 10% sodium hydroxide solution (20 c.c.), was shaken with methyl sulphate (3 c.c.), added in portions, a homogeneous solution was obtained, from which on acidification 4-methoxydimethylphthalide was precipitated; after being washed with dilute alkali (in which it was now insoluble) and recrystallised from aqueous methyl alcohol, it melted at 100° (Found: C, 68.5; H, 6.4.  $C_{11}H_{12}O_3$  requires C, 68.7; H, 6.3%).

4-Hydroxydimethylphthalide can be distilled in a vacuum and is unaffected by prolonged boiling with concentrated hydrochloric acid, 50% (by weight) sulphuric acid, or by fusion with potassium hydroxide below *ca.* 250°. On fusion with potassium hydroxide for 10 minutes at 280–300°, acetone, *m*-hydroxybenzoic acid, and some phenol were obtained.

4-Hydroxy-N-phenyl- $\alpha$ -dimethylphthalimidine (X).—4-Hydroxydimethylphthalide (2 g.) and aniline (10 c.c.) were heated for 2 hours at 300°. The violet liquid obtained was diluted with ether, and the aniline removed by dilute acid. The 4-hydroxy-N-phenyl- $\alpha$ -dimethylphthalimidine, which was only partly dissolved in the ether, was shaken into dilute sodium hydroxide solution and obtained on acidification as a pale blue powder. It crystallised from a little ethyl alcohol with one molecule of water of crystallisation (Found: C, lost; H, 6.3;  $H_2O$ , 6.5.  $C_{16}H_{15}O_2N \cdot H_2O$  requires H, 6.3;  $H_2O$ , 6.6%); or, better, from methyl alcohol, from which it formed colourless pseudo-rhombic crystals (showing well-developed domal faces), containing one molecule of methyl alcohol of crystallisation (Found: MeOH, 11.7; C, 71.4; H, 6.8. Found in dried material: C, 76.05; H, 6.1.  $C_{16}H_{15}O_2N \cdot MeOH$  requires C, 71.6; H, 6.7; MeOH, 11.2%.  $C_{16}H_{15}O_2N$  requires C, 75.85; H, 6.0%). Both crystalline forms and the anhydrous material melt at 214–215°.

The same substance was formed on heating 4-hydroxydimethylphthalide (1 g.) with aniline (5 c.c.) and aniline hydrochloride (5 g.) for 2 hours at 210° (but not on refluxing with aniline alone). In this case, however, considerably more of the coloured impurity

(possibly the phenylimide of X) was formed. On distillation with soda-lime, aniline was evolved in quantity.

The *acetoxy*-derivative was prepared (a) from the crystallised material by warming on the water-bath for 1 hour with ten times the quantity of acetic anhydride, and (b) from the dried material by the pyridine and acetyl chloride method. After crystallisation from methyl alcohol, both specimens, alone or mixed, melted at 219° (Found: C, 73·3; H, 5·9.  $C_{18}H_{17}O_3N$  requires C, 73·2; H, 5·8%). Mixed with the hydroxy-compound, the substance melted from 174° to 198°.

3 : 5-Dibromo-4-hydroxy- $\alpha\alpha$ -dimethylphthalide.—When bromine (0·9 g.) in a little acetic acid was gradually added to 4-hydroxy-dimethylphthalide (0·5 g.) in 50% acetic acid (10 c.c.), and the mixture kept for 30 minutes, 3 : 5-dibromo-4-hydroxy- $\alpha\alpha$ -dimethylphthalide (0·72 g.; 76% yield) separated. Recrystallised from 50% acetic acid, it formed plates with one molecule of water of crystallisation, which did not melt sharply. When dried, it melted at 125° (Found:  $H_2O$ , 5·2. Found in dried material: Br, 47·6.  $C_{10}H_8O_3Br_2 \cdot H_2O$  requires  $H_2O$ , 5·1%.  $C_{10}H_8O_3Br_2$  requires Br, 47·6%).

The author is very greatly indebted to Professor Sidney Smith, late Director of the Medico-Legal Section, Ministry of Justice, Cairo, for a supply of hashish, which enabled this investigation to be undertaken.

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## CXXII.—*The Preparation of Secondary Alkylaryl-amines and their Purification.*

By WILFRED JOHN HICKINBOTTOM.

THE isolation of the pure secondary amine from the products of interaction of an alkyl halide and a primary arylamine can be economically and conveniently accomplished by the following process. The alkyl bromide is heated with an excess (usually  $2\frac{1}{2}$ —4 mols.) of the primary aromatic amine. The tendency for the alkyl halide to yield tertiary amine is thus repressed and the product consists almost entirely of the secondary amine and the excess of the primary amine combined with the hydrogen bromide liberated in the reaction. The separation of the primary and secondary



amines is effected by Morgan's method (E.P. 102,834, 1916) depending on the formation of sparingly soluble additive compounds of zinc chloride and aniline or its homologues of the general formula  $B_n \cdot ZnCl_2$ . The alkylanilines do not form compounds with zinc chloride in the presence of water (compare Reilly and Hickinbottom, J., 1920, 117, 127).

It has now been found that the excess of aniline or *m*-xylydine can be completely precipitated by the addition of a 50% solution of zinc chloride to the mixture of amines liberated from the product of the reaction between the primary amine and the alkyl halide; the uncombined secondary amine is isolated by draining the precipitated zincchloride and extracting with light petroleum. The yield of secondary amines thus obtained from *n*-propyl, isopropyl, and *n*-butyl bromides was upwards of 70% of the theoretical, calculated on the weight of the alkyl halide; frequently it was of the order of 75—85%. Further purification to remove small quantities of tertiary amines consisted in converting the crude secondary amine into its hydrobromide and crystallising this from alcohol (for *n*-butylaniline hydrobromide, benzene is a better solvent). Another method, also employed for ethyl-, *n*-propyl-, and isopropyl-anilines, was to prepare the acetyl derivative, which after distillation and crystallisation yielded the pure secondary amine on hydrolysis.

The yield of isobutylaniline obtained by the method now described was always small (30—40%). This is due, in part at least, to the presence of *tert*.-butyl bromide in the isobutyl bromide. According to Michael, Scharf, and Voigt (*J. Amer. Chem. Soc.*, 1916, 38, 653) this is a normal impurity in isobutyl bromide, and one very difficult to remove. It does not, however, affect the purity of the isobutylaniline, as the tertiary bromide yields butylene when warmed with aniline (compare Nef, *Annalen*, 1899, 309, 164).

#### EXPERIMENTAL.

*n*-Propylaniline.—Aniline (230 g.;  $2\frac{1}{2}$  mols.) was heated with *n*-propyl bromide (1 mol.) under reflux in a boiling water-bath for 5 hours, the product was rendered alkaline, and the amines were separated and treated with a solution of 150 g. of zinc chloride in 150 g. of water. The mixture, when cooled and stirred, was rapidly converted into a thick paste which, after 12 hours, was drained on a large Buchner funnel, washed with cold water, pressed to remove as much as possible of the water, and extracted several times with boiling light petroleum. The extracts were combined, washed with water and with dilute aqueous ammonia, and dried over potassium carbonate. Removal of the solvent left *n*-propylaniline,

which was obtained almost pure after two distillations: yield, 94.5 g. (70%); b. p. 218—222°. A further quantity (10 g.), collected between 222° and 230°, contained an appreciable amount of the tertiary amine.

A very convenient method of preparing aceto-*n*-propylanilide consisted in distilling equal weights of the secondary amine and acetic anhydride: the distillate collected between 240° and 265° and once crystallised from light petroleum was pure aceto-*n*-propylanilide, m. p. 48—49°.

*iso*Propylaniline, b. p. 206—208° (yield, 73%), was prepared in the same way from aniline and *isopropyl* bromide and freed from traces of tertiary amine by conversion into its acetyl derivative, m. p. 42°, and subsequent hydrolysis.

*n*-Butylaniline.—Aniline (130 g.) and *n*-butyl bromide (70 g.), heated in a boiling water-bath for 3 hours, gave, after removal of the excess of aniline by Morgan's method, approximately pure *n*-butylaniline (57 g.; yield, 75%). After purification through the hydrobromide, the amine had b. p. 235—235.5°/744 mm. (yield, 38 g.; 50%). A further quantity was obtained by fractional crystallisation of the mother-liquor of the hydrobromide.

*iso*Butylaniline.—*iso*Butyl bromide (prepared by heating *iso*-butyl alcohol with concentrated hydrobromic acid: it contained some *tert*.-butyl bromide) (120 g.) was heated with aniline (2½ mols.) in a boiling water-bath for 2 hours, and the excess of aniline subsequently removed as described above. The crude *isobutylaniline* gave the following fractions on distillation: 225°, 9 g.; 225—227°, 26 g.; 227—231°, 20 g.

Pure *isobutylaniline* was obtained by converting the crude product into hydrobromide by the addition of concentrated hydrobromic acid, crystallising the salt from absolute alcohol, and decomposing it with aqueous sodium hydroxide. The amine was characterised by its *p*-toluenesulphonyl derivative, which crystallised from alcohol in slender prismatic needles, m. p. 122—123° (Found: N, 4.7.  $C_{17}H_{21}O_2NS$  requires N, 4.6%).

The author desires to thank Mr. R. G. Ault and Mr. S. E. A. Ryder for their assistance in the experimental work.

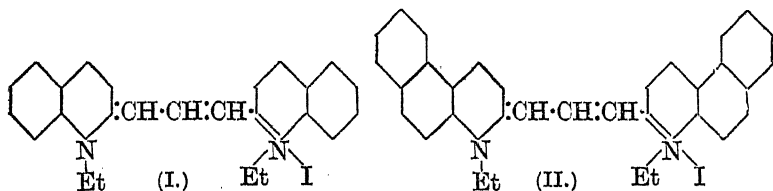
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EDGBASTON.

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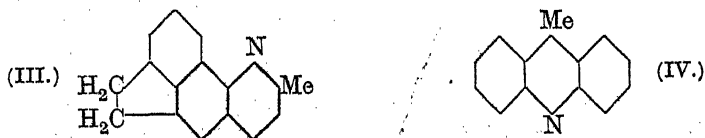
CXXIII.—*Attempts to prepare Cyanine Dyes from Quaternary Salts of 2-Methylacenaphthpyridine and of 5-Methylacridine.*

By FRANCES MARY HAMER.

WITH any class of dye, there is a tendency for increase in molecular weight to be accompanied by a shift of the absorption bands towards the red end of the spectrum. Where the dyes are photographic sensitisers, there is a corresponding shift of the maxima of extra-sensitisation. Dyes which sensitise further into the red should therefore be obtainable by replacing the nuclei of known sensitisers by heavier nuclei. An example of the shift which occurs with increase in molecular weight is afforded by comparison of pina-cyanol (I), for which the maximum of the chief sensitising band lies at  $\lambda$  6375 Å., with the carbocyanine (II), which has its sensitising



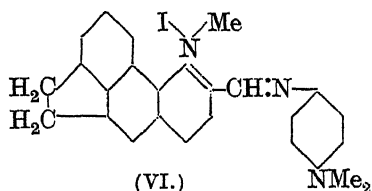
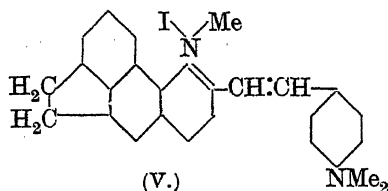
maximum at  $\lambda$  6900 Å. (Mees and Gutekunst, *J. Ind. Eng. Chem.*, 1922, 14, 1060). So also, the cyanine dyes recently prepared from quaternary salts of methyl- $\alpha$ - and - $\beta$ -naphthathiazoles show absorption further towards the red than the corresponding dyes prepared from salts of methylbenzthiazole, the shift being greater with the thiocarbocyanines, where two benzthiazole nuclei are replaced by two naphthathiazole nuclei, than with the thio- $\psi$ -cyanines, where there is only one such replacement (Hamer, J., 1929, 2598). In this connexion it seemed of interest to prepare quaternary salts of 2-methylacenaphthpyridine (III) and of 5-methylacridine (IV) in order to see whether such salts would give rise to cyanine dyes and, if so, to examine the photographic properties of the latter.



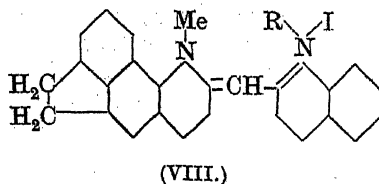
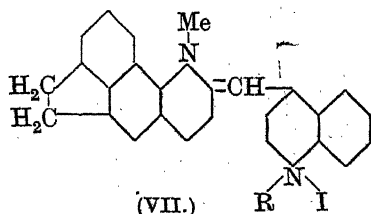
2-Methylacenaphthpyridine has been prepared from 3-aminoacenaphthene. Sachs and Mosebach's original method for reducing 3-nitroacenaphthene (*Ber.*, 1911, 44, 3855), used also by Stewart (*J.*, 1925, 427, 1331), has been said by Fleischer and Schranz to

give only a 20% yield, the chief product being the sodium salt of *N*-acenaphthyl-3-sulphaminic acid (*Ber.*, 1922, **55**, 3253); their observation that this salt remains in solution was not confirmed. Their method of preparation (see also Morgan and Stanley, *J. Soc. Chem. Ind.*, 1924, **43**, 343T) was adopted, with very slight modification. The preparation, from 3-aminoacenaphthene, by the action of paraldehyde and hydrochloric acid, of 2-methylacenaphthpyridine has been described by Nair and Simonsen (*J.*, 1926, 3140). But as they proceed, without removal of the tar which accompanies the condensation product, to treat the reaction mixture with alkali, modification was required. Comparative experiments showed the large excess of paraldehyde and of hydrochloric acid to be unnecessary, as also is the protracted time of heating.

The *methiodide* of 2-methylacenaphthpyridine was prepared, but similar conditions gave only a trace of the corresponding ethiodide. The methiodide condenses with *p*-dimethylaminobenzaldehyde and with *p*-nitrosodimethylaniline: as in analogous cases (Hamer, *J.*, 1924, **125**, 1348; 1929, 2598), the former product (V) is a sensitiser and the latter (VI) a desensitiser. 2-Methylacenaphthpyridine



methiodide reacts with quinoline methiodide or ethiodide to give an isocyanine (VII) and with 2-iodoquinoline methiodide or ethiodide to give a *ψ*-cyanine (VIII), the latter condensation proceeding better in aqueous solution than in the more generally applicable alcoholic



solution (compare Hamer, *J.*, 1928, 206). Comparison of the absorption bands of these new cyanines, in alcoholic solution, with those of the parent dyes reveals a shift of 150 Å. towards the red. Mr. O. F. Bloch found the compounds to be photographic sensitisers, but of no outstanding merit. It is remarkable, in view of its reactivity, that 2-methylacenaphthpyridine methiodide does not yield

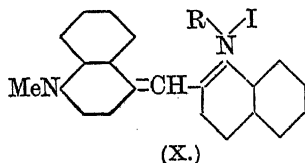
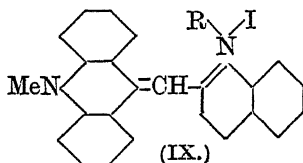
a carbocyanine by the ethyl orthoformate and pyridine method (Hamer, J., 1927, 2796); the use of acetic anhydride as solvent is no more successful.

5-Methylacridine has previously been prepared from diphenylamine by the action of acetonitrile or acetic acid (Bernthsen, *Annalen*, 1878, **192**, 29; Fischer and Rudolph, *Ber.*, 1882, **15**, 1500; Besthorn and Fischer, *Ber.*, 1883, **16**, 68; Bernthsen and Bender, *ibid.*, p. 1802; Fischer, *ibid.*, p. 1820; Bernthsen, *Annalen*, 1884, **224**, 1). In the present work, however, it was prepared from acetyldiphenylamine, by heating it with zinc chloride in a sealed tube; it was conveniently isolated as its tartrate, by Koenigs' method (*Ber.*, 1899, **32**, 3599).

5-Methylacridine methiodide has been prepared by Bernthsen (*Annalen*, 1884, **224**, 1), by Decker (*Ber.*, 1905, **38**, 2493), by Freund and Bode (*Ber.*, 1909, **42**, 1746), and by Kaufmann and Albertini (*Ber.*, 1911, **44**, 2052). Except for the statement of the last-named authors, that the dust of the methiodide attacks the breathing organs, there is no reference to the strong sternutatory action which is the most striking characteristic of this salt.

Now the reactivity of the methyl group in 5-methylacridine itself is manifested by its condensation with (a) chloral (Bernthsen and Muhlert, *Ber.*, 1887, **20**, 1541), (b) benzaldehyde and its *m*- and *p*-nitro-derivatives (Friedländer, *Ber.*, 1905, **38**, 2840; Porai-Koschitz, *Z. Farb. Text.-ind.*, 1907, **6**, 291), (c) *p*-nitrosodimethylaniline (Kaufmann and Vallette, *Ber.*, 1912, **45**, 1736), and (d) formaldehyde (Koenigs, *loc. cit.*; Homberger and Jensen, *J. Amer. Chem. Soc.*, 1926, **48**, 800). Since the quaternary salts of a base containing a reactive methyl group are, in general, more reactive than is the base itself (Mills and Smith, J., 1922, **121**, 2724), it was both surprising and interesting to obtain a series of negative results in the case of 5-methylacridine methiodide. For instance, it did not react (a) with ethyl orthoformate in the presence of pyridine to give a carbocyanine, (b) with quinoline methiodide in aqueous-alcoholic solution, under the influence of sodium hydroxide, to give an isocyanine, (c) with *p*-dimethylaminobenzaldehyde, in absolute alcoholic solution and in the presence of piperidine, or (d) with *p*-nitrosodimethylaniline, under similar conditions. (e) An attempt to effect condensation between it and 2-iodoquinoline methiodide by the normal procedure, absolute alcohol being used as solvent and potassium hydroxide as condensing agent (Hamer, J., 1928, 206), also gave a negative result. But when water was employed as the solvent medium, condensation between 5-methylacridine methiodide and 2-iodoquinoline methiodide or ethiodide took place. Although these new dyes (IX) may be regarded as

derived from the simple *isocyanine* (X), their absorption spectra are of a different character, showing one broad band, with an ill-



defined maximum, whereas the latter has two well-marked, relatively narrow bands. The maximum of this broad band is in approximately the same position as that of the chief band of the parent *isocyanine*, instead of showing the expected shift towards the red. Both the new dyes are entirely devoid of sensitising properties.

#### EXPERIMENTAL.

**3-Aminoacenaphthene.**—A mixture of 3-nitroacenaphthene (40 g.) with spirit (400 c.c.) and water (200 c.c.) was boiled in a flask (3 l. capacity). It was removed from the water-bath for the addition of sodium hydrosulphite (100 g.) in three portions, reaction occurring at each addition. After 15 minutes' boiling, the spirit was distilled off and the residue treated with water (500 c.c.) and boiled. When cold, the solid was filtered off, ground to a paste with water, and hydrolysed by heating on the water-bath with concentrated hydrochloric acid (300 c.c.) and water (1200 c.c.). The violent bumping, which occurs on boiling, does not take place on the water-bath, and the isolation of the solid before hydrolysis has the advantage of avoiding the copious evolution of sulphur dioxide, caused by addition of the acid to the reaction mixture, both these being points whereby the earlier method has been modified. The liquid was filtered hot, to remove a little black matter, and the filtrate was made alkaline with ammonia. The yield of base, after washing with water and drying, was 63–64%, and, after recrystallisation from petrol, 49–53%. M. p. 107°.

**2-Methylacenaphthpyridine.**—3-Aminoacenaphthene (40 g.; 1 mol.) was treated with hydrochloric acid ( $d$  1.19; 40 c.c.) and paraldehyde (26 c.c.; 2.5 mols.). The flask was cooled with water in order to abate the violence of the reaction, which occurs without the application of external heat. Finally it was heated on the water-bath for  $\frac{1}{2}$ -hour and water (1 l.) was added. When cold, the mixture was filtered from tar, and the filtrate and washings were treated with excess of ammonia. The aqueous liquid was poured off from the semi-solid base and the latter was twice extracted with hot 10% sulphuric acid (80 + 40 c.c.), the extract being filtered hot. The yellow sulphate, which slowly crystallised from the filtrate, was

collected, washed with acetone (31.9 g. obtained), dissolved in hot water, and treated with ammonia. The crude base (20.3 g.) was obtained in 39% yield and after recrystallisation from spirit the yield (15.2 g.) was 29%. M. p.  $131^{\circ}$ , as recorded by Nair and Simonsen (*loc. cit.*).

*2-Methylacenaphthpyridine Methiodide.*—2-Methylacenaphthpyridine (10 g.) and methyl iodide (10 c.c.) were heated in a sealed tube at  $100^{\circ}$  for 2 days. The product was extracted with ether; the undissolved residue (12.8 g.; 78% yield) separated from spirit in orange crystals (62% yield), m. p. about  $212^{\circ}$ . A specimen was dried in a vacuum desiccator before analysis, the method of Carius being used in this, and in all subsequent halogen determinations, except where otherwise stated (Found: I, 35.0.  $C_{17}H_{16}NI$  requires I, 35.2%).

*2-p-Dimethylaminostyrylacenaphthpyridine Methiodide (V).*—2-Methylacenaphthpyridine methiodide (3 g.; 1 mol.) and *p*-dimethylaminobenzaldehyde (1.24 g.; 1 mol.), dissolved in hot 99% spirit (300 c.c.), were treated with piperidine (0.5 c.c.) and the mixture was boiled for 5 hours. The solid was filtered off when cold, and the filtrate concentrated to  $\frac{1}{3}$  volume in order to obtain a second crop (total yield, 2.9 g.). The product was twice boiled out with methyl alcohol ( $2 \times 50$  c.c.), and the undissolved residue recrystallised from spirit (750 c.c.). The *methiodide* (V) (24% yield) was again recrystallised and was dried for analysis in a vacuum at  $100$ – $120^{\circ}$  (Found: I, 25.5.  $C_{26}H_{25}N_2I$  requires I, 25.8%). The green crystals melt at  $224^{\circ}$  (decomp.). The spirit solution has a wide absorption band with its maximum at about  $\lambda$  5200 Å. A plate bathed in this solution acquires a feeble extra sensitivity, extending to  $\lambda$  7100 Å., but the dye is less effective when added to the emulsion.

*p-Dimethylaminoanil of Acenaphthpyridine-2-aldehyde Methiodide (VI).*—2-Methylacenaphthpyridine methiodide (3 g.; 1 mol.) and *p*-nitrosodimethylaniline (1.25 g.; 1 mol.) were boiled in absolute alcoholic solution (50 c.c.), with addition of piperidine (2 drops), for 6 hours. The product (3.2 g.; 78% yield) was recrystallised from methyl alcohol (1500 c.c.; 2.05 g. obtained; 50% yield). After a second recrystallisation the olive-green crystals, m. p.  $195^{\circ}$  (decomp.), were dried for analysis in a vacuum at  $60$ – $80^{\circ}$  (Found: I, 25.4.  $C_{25}H_{24}N_3I$  requires I, 25.7%). The compound desensitises photographic plates more powerfully than does safranin, but is of no practical use because its desensitising action is destroyed by the sulphite and carbonate of the developer.

*isoCyanine (VII) from 2-Methylacenaphthpyridine Methiodide and Quinoline Methiodide.*—2-Methylacenaphthpyridine methiodide

(6 g.; 1 mol.) and quinoline methiodide (9.0 g.; 2 mols.) were boiled with absolute alcohol (300 c.c.) and the mixture was treated with sodium (0.46 g.; 1.2 mols.), dissolved in absolute alcohol (30 c.c.), and then boiled for 15 minutes. The solid (5.5 g.), which separated on cooling, was twice boiled out with methyl alcohol (50 + 100 c.c.), and the undissolved residue was recrystallised from methyl alcohol. The small green crystals (1.17 g.; 14% yield) obtained from this third fraction were again recrystallised from methyl alcohol (200 c.c.; 0.83 g. obtained; 10% yield). The *isocyanine* was dried in a vacuum at 60–80° (Found: C, 64.2; H, 5.0; I, 25.1.  $C_{27}H_{23}N_2I$  requires C, 64.5; H, 4.6; I, 25.3%). When it is heated, a change occurs between 160° and 170° and, if heating is rapid, the dye even melts; if slowly heated, melting with decomposition occurs between 220° and 240°, the exact point depending upon the rate of rise of temperature. The chief absorption band of the spirit solution has its maximum at  $\lambda$  5750 Å., and there is another maximum at  $\lambda$  5400 Å. A plate bathed in the solution shows a very uniform band of extra sensitisation, extending to  $\lambda$  6800 Å. for moderate exposures and with maxima at  $\lambda$  6100 Å. and  $\lambda$  5400 Å.

*isoCyanine from 2-Methylacenaphthpyridine Methiodide and Quinoline Ethiodide.*—Similarly, 2-methylacenaphthpyridine methiodide (6 g.) was condensed with quinoline ethiodide (9.47 g.) and the resultant dye (4.85 g.) was extracted with ether. The undissolved residue (4.5 g.) was boiled with insufficient methyl alcohol (50 c.c.) to dissolve it; the residue was recrystallised from methyl alcohol (200 c.c.), giving green crystals, m. p. about 217° (decomp.), in 16% yield (1.39 g.). They were dried for analysis in a vacuum at 100–110° (Found: I, 24.7.  $C_{28}H_{25}N_2I$  requires I, 24.6%). The chief absorption band of the spirit solution lies at  $\lambda$  5850 Å. and the secondary one at  $\lambda$  5400 Å. The sensitising action conferred on a plate bathed in a solution of the dye extends to  $\lambda$  6600 Å., and is not quite so uniform as that of the preceding compound, showing a distinct gap at  $\lambda$  5000 Å. One maximum, at  $\lambda$  6050 Å., is more strongly marked than the other, which is at  $\lambda$  5500 Å.

*$\psi$ -Cyanine (VIII) from 2-Methylacenaphthpyridine Methiodide and 2-Iodoquinoline Methiodide.*—Crude 2-iodoquinoline methiodide (8 g.; 1 mol.) was added to boiling water (500 c.c.), and a little undissolved periodide filtered off. 2-Methylacenaphthpyridine methiodide (7.27 g.; 1 mol.) was added, followed by an aqueous solution (40 c.c.) of potassium hydroxide (3.0 g.; 2.4 mols.), and boiling was continued for 5 minutes. The resultant solid was purified by boiling out with water and the residue (3.8 g.) was extracted with ether in a Soxhlet apparatus. The undissolved



residue (3.6 g.) was recrystallised from methyl alcohol (750 c.c.; 2.1 g. obtained; 21% yield). After a second recrystallisation from methyl alcohol (400 c.c. for 1.9 g., giving 1.2 g.; 13% yield), the  $\psi$ -cyanine was dried in a vacuum at 60–80° (Found: I, 24.9.  $C_{27}H_{23}N_2I$  requires I, 25.3%). The compact bronze crystals melt at 236° (decomp.). With a spirit solution, the chief absorption band has its crest at  $\lambda$  5400 Å.: the second band, which is almost as strong, has its crest at  $\lambda$  5100 Å. On bathing plates, a band of extra sensitisation is conferred, extending to  $\lambda$  6400 Å. for moderate exposures, and with its maximum at  $\lambda$  5700 Å.

*$\psi$ -Cyanine from 2-Methylacenaphthpyridine Methiodide and 2-Iodoquinoline Ethiodide.*—From 2-iodoquinoline ethiodide (4 g.) and 2-methylacenaphthpyridine methiodide (3.51 g.), the  $\psi$ -cyanine, similarly precipitated by the action of potassium hydroxide, was at first obtained in the form of a tar, which improved during boiling and hardened when cold. It was extracted with hot water and the residue (2.44 g.) was extracted with ether in a Soxhlet apparatus. That residue (2.33 g.) was recrystallised from methyl alcohol (200 c.c.; 1.32 g. obtained; 26% yield). It was dried for analysis in a vacuum at 100–110° (Found: I, 24.4.  $C_{28}H_{25}N_2I$  requires I, 24.6%). The dye forms small brownish-red crystals, m. p. 201° (decomp.). The principal absorption band is at  $\lambda$  5450 Å. and there is another at 5100 Å. It exerts a powerful sensitising action on plates bathed in its solution; the action extends to  $\lambda$  6400 Å. for moderate exposures and shows maxima at  $\lambda$  5700 Å. and 5100 Å.

*Acetyldiphenylamine.*—Diphenylamine has been acetylated by means of acetyl chloride (Meister, *Ber.*, 1872, 5, 283; Merz and Weith, *Ber.*, 1873, 6, 1511) and by acetic anhydride (Claus, *Ber.*, 1881, 14, 2365). In a modification of the latter method, diphenylamine (30 g.), acetic anhydride (60 c.c.), and fused sodium acetate (30 g.) were heated together on the water-bath for 1½ hours and the product was treated with water and ammonia. After recrystallisation from very dilute spirit, the base was obtained in 80% yield. It melted at 84–85° with previous softening, but lost solvent of crystallisation on drying on the water-bath and in a vacuum desiccator; the anhydrous substance melted at 101–102°. Meister, and Merz and Weith, give m. p. 99.5°, Claus gives m. p. 103°, and Wallach (*Annalen*, 1882, 214, 234) gives m. p. 101–102°.

*5-Methylacridine.*—A mixture of acetyldiphenylamine (5 g.) with five times its weight of powdered zinc chloride was heated in a sealed tube at 220–240° for 6½ hours. The dark mass was extracted with hot 50% sulphuric acid and the extract was treated with water and excess of ammonia to precipitate the base. This was extracted with benzene and, after removal of the solvent, the

residue was dissolved in hot spirit and treated, as by Koenigs (*loc. cit.*), with a hot solution of tartaric acid (5 g.) in spirit (50 c.c.). The tartrate (6.9 g.) was suspended in cold water and treated with excess of sodium carbonate solution and the base was extracted with ether, the extract being dried with potassium hydroxide. The residue (74% yield) after removal of the solvent was recrystallised from dilute spirit and dried on the water-bath and in a vacuum desiccator (46% yield). M. p. 117—118° as found by Koenigs (*loc. cit.*); Decker's observation (*loc. cit.*) as to the low m. p. before removal of solvent of crystallisation was confirmed.

**5-Methylacridine Methiodide.**—5-Methylacridine (3.7 g.) and methyl iodide (3.7 c.c.) were heated for 2 days in a sealed tube at 100°. The product was extracted with ether, and the undissolved residue (5.9 g.; 92% yield) recrystallised from water (about 300 c.c.; 4.1 g. obtained; 64% yield). It was dried in the steam-oven before analysis; a solution in dilute sulphuric acid was treated with silver nitrate (Found: I, 37.8. Calc. for  $C_{15}H_{14}NI$ : I, 37.9%). Melting with decomposition occurred at about 263°. Bernthsen (*Annalen*, 1884, 224, 1) gives m. p. 185° (decomp.), Freund and Bode (*loc. cit.*) give m. p. 273—275°, and Kaufmann and Albertini (*loc. cit.*) give m. p. 235—245°, with decomposition from 200°.

**1:1'-Dimethyl-2:3(or 2':3')-benzisocyanine Iodide (IX; R = Me).**—5-Methylacridine methiodide (1 g.; 1 mol.) and 2-iodoquinoline methiodide (1.2 g.; 1 mol.) were added to boiling water (60 c.c.), potassium hydroxide (0.4 g.; more than 2 mols.) dissolved in water (10 c.c.) was added, and the mixture was boiled for 5 minutes. The blue tar produced, which solidified on cooling, was filtered off and extracted with ether. The undissolved residue (0.84 g.; 59% yield) was recrystallised from methyl alcohol (40 c.c.), the *iodide* (IX) being thus obtained in 25% yield (0.36 g.). It was dried in a vacuum at 100—110° before analysis (Found: I, 26.8.  $C_{25}H_{21}N_2I$  requires I, 26.65%). It forms long crystals with a bronze lustre. M. p. about 250—265°, but the exact point is quite indefinite, since decomposition begins at about 230°. Its spirit solution has a broad absorption band extending from  $\lambda$  4700 Å. to 6200 Å., and with a maximum at about 5500 Å.

**1(or 1')-Methyl-1'(or 1)-ethyl-2:3(or 2':3')-benzisocyanine iodide** was similarly prepared from 5-methylacridine methiodide (3 g.) and 2-iodoquinoline ethiodide (3.68 g.). After ether extraction, the undissolved residue (3.05 g.) was dissolved in hot chloroform (800 c.c.). The solution was concentrated and from it, on cooling, the dye was obtained in crystalline form (2.0 g.). It was recrystallised from methyl alcohol (40 c.c.) and was thus obtained in 29% yield (1.25 g.). It was again recrystallised from methyl alcohol

and was dried for analysis in a vacuum at 100—110° (Found : I, 25.8.  $C_{26}H_{23}N_2I$  requires I, 25.9%). It forms lustrous dark green crystals, which soften at 150—160° but do not melt until about 232°; if they are put into a bath at 160°, however, melting occurs at once. The absorption of the spirit solution is very like that of the preceding dye.

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### CXXIV.—*Tetrachloroiodides of the Alkaloids.*

By FREDERICK DANIEL CHATTAWAY and GEORGE DAVID PARKES.

MANY of the commoner alkaloids yield well-characterised tetrachloroiodides when a solution of the alkaloid in concentrated hydrochloric acid is added to excess of a solution of tetrachloroiodic acid made by saturating with chlorine a suspension of finely powdered iodine in concentrated hydrochloric acid.

These alkaloidal tetrachloroiodides are all decomposed by a solution of sodium sulphite, the base being liberated. When they are treated with a solution of potassium iodide acidified with acetic acid, iodine is quantitatively liberated. This reaction has been used for the analysis of these compounds.

Hexamethylenetetramine also forms a stable tetrachloroiodide.

The tetrachloroiodides of many quaternary bases are easily made by saturating a solution of the iodide in concentrated hydrochloric acid with chlorine.

#### EXPERIMENTAL.

The solution of tetrachloroiodic acid used was obtained by suspending finely powdered iodine (15 g.) in concentrated hydrochloric acid (80 c.c.) and saturating it with chlorine.

*Quinine Tetrachloroiodide*,  $C_{20}H_{24}O_2N_2 \cdot 2HICl_4$ .—When a solution of 10 g. of quinine hydrochloride in 50 c.c. of concentrated hydrochloric acid was added to 60 c.c. of tetrachloroiodic acid solution, *quinine tetrachloroiodide* separated immediately as a bright yellow, microcrystalline powder. This was filtered off and dissolved in 150 c.c. of boiling glacial acetic acid, the solution was cooled, and 300 c.c. of concentrated hydrochloric acid were added; the tetrachloroiodide thus obtained, after being dried in a desiccator over phosphoric oxide and a few lumps of lime, melted at 114° (decomp.) (Found : Cl, 32.3.  $C_{20}H_{26}O_2N_2Cl_8I_2$  requires Cl, 32.9%).

*Cinchonine tetrachloroiodide*,  $C_{19}H_{22}ON_2 \cdot 2HICl_4$ , was similarly pre-

pared and purified. It separated as a bright yellow, microcrystalline powder, m. p.  $85^{\circ}$  (decomp.) (Found: Cl, 33.4.  $C_{19}H_{24}ON_2Cl_3I_2$  requires Cl, 34.0%).

*Strychnine Tetrachloroiodide*,  $C_{21}H_{22}O_2N_2.HCl_4$ .—A solution of 5 g. of strychnine in 20 c.c. of chloroform was saturated with hydrogen chloride and added to the solution formed by dissolving 3 g. of iodine in 20 c.c. of chloroform and saturating it with chlorine. *Strychnine tetrachloroiodide* separated at once as a pale yellow, microcrystalline powder, m. p.  $91^{\circ}$  (decomp.) (Found: Cl, 23.3.  $C_{21}H_{23}O_2N_2Cl_4I$  requires Cl, 23.5%).

*Morphine tetrachloroiodide*,  $C_{17}H_{19}O_3N.HCl_4$ , was prepared from 5 g. of morphine hydrochloride, dissolved in 40 c.c. of concentrated hydrochloric acid, and 10.5 c.c. of tetrachloroiodic acid solution. It crystallised from glacial acetic acid, in which it was very easily soluble, in small, pale orange needles, which melt at  $78^{\circ}$  (decomp.), and rapidly decompose when kept, even in a sealed tube (Found: Cl, 25.4.  $C_{17}H_{20}O_3NCl_4I$  requires Cl, 25.6%).

*Codeine tetrachloroiodide*,  $C_{18}H_{21}O_3N.HCl_4$ , was prepared similarly from 2 g. of codeine, dissolved in 20 c.c. of concentrated hydrochloric acid, and 4.5 c.c. of tetrachloroiodic acid solution. It crystallised from glacial acetic acid, containing a little iodine trichloride, in which it was easily soluble, in pale orange needles, but it was not found possible to dry the compound without slight decomposition occurring.

*Cocaine Tetrachloroiodide*,  $C_{17}H_{21}O_4N.HCl_4$ .—When a solution of 1 g. of cocaine hydrochloride in 5 c.c. of concentrated hydrochloric acid was added to 5 c.c. of tetrachloroiodic acid solution prepared as above, *cocaine tetrachloroiodide* separated as a bright yellow solid. It crystallised from glacial acetic acid, containing a little iodine trichloride, in which it was moderately easily soluble, in small, pale yellow, irregular, flat plates, m. p.  $141^{\circ}$  (decomp.) (Found: Cl, 25.3.  $C_{17}H_{22}O_4NCl_4I$  requires Cl, 24.75%).

*Hexamethylenetetramine tetrachloroiodide*,  $(CH_2)_6N_4.HCl_4$ , separated in bright yellow prisms, m. p.  $147^{\circ}$  (decomp.), when a solution of 5 g. of hexamethylenetetramine in 25 c.c. of concentrated hydrochloric acid was added to 30 c.c. of tetrachloroiodic acid solution (Found: Cl, 34.2.  $C_6H_{13}N_4Cl_4I$  requires Cl, 34.6%). It cannot be recrystallised, as when heated with glacial acetic acid it decomposes into formaldehyde and ammonium tetrachloroiodide.

*1-Methylpyridine Tetrachloroiodide*,  $C_5H_5NMeI_4$ .—5 G. of pyridine methiodide were dissolved in 25 c.c. of concentrated hydrochloric acid and a stream of chlorine was passed through the cooled solution. Iodine at first separated, but gradually disappeared and the bright yellow *1-methylpyridine tetrachloroiodide* separated.

It crystallised from boiling glacial acetic acid containing a little iodine trichloride, in which it was sparingly soluble, in clusters of small yellow needles, m. p.  $180^{\circ}$  (decomp.) (Found: Cl, 39.0.  $C_6H_8NCl_4I$  requires Cl, 39.1%).

1:2-*Dimethylpyridine tetrachloroiodide* separates from boiling glacial acetic acid, in which it is rather sparingly soluble, in bright yellow, irregular, twinned plates, m. p.  $185^{\circ}$  (decomp.) (Found: Cl, 37.5.  $C_7H_{10}NCl_4I$  requires Cl, 37.7%).

1:2:4:6-*Tetramethylpyridine tetrachloroiodide* separates from boiling glacial acetic acid, in which it is fairly easily soluble, in bright yellow, irregular, flat plates, m. p.  $130^{\circ}$  (decomp.) (Found: Cl, 35.2.  $C_9H_{14}NCl_4I$  requires Cl, 35.1%).

1-*Methylquinoline tetrachloroiodide* separates from glacial acetic acid, in which it is somewhat sparingly soluble, in pale yellow prisms, m. p.  $191^{\circ}$  (Found: Cl, 34.15.  $C_{10}H_{10}NCl_4I$  requires Cl, 34.4%).

6-*Chloro-1-methylquinoline tetrachloroiodide* separates from boiling glacial acetic acid, in which it is sparingly soluble, in long yellow needles, m. p.  $167^{\circ}$  [Found: Cl (added), 31.7.  $C_{10}H_9NCl_5I$  requires Cl (added), 31.7%].

6-*Bromo-1-methylquinoline tetrachloroiodide* crystallises from glacial acetic acid in bright yellow needles, m. p.  $176^{\circ}$  (Found: Cl, 29.1.  $C_{10}H_9NCl_4BrI$  requires Cl, 28.9%).

N-*Methylstrychnine tetrachloroiodide* separates from glacial acetic acid, in which it is moderately easily soluble, in minute, pale yellow needles which, when heated, decompose without melting (Found: Cl, 22.9.  $C_{22}H_{25}O_2N_2Cl_4I$  requires Cl, 23.0%).

NN-*Dimethylnicotine bistetrachloroiodide* separates from boiling glacial acetic acid, in which it is somewhat sparingly soluble, in fine yellow needles, m. p.  $145^{\circ}$  (Found: Cl, 38.6.  $C_{12}H_{20}N_2Cl_8I_2$  requires Cl, 38.9%).

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## CXXV.—*The Properties of the Chlorides of Sulphur. Part IV. Density and Surface Tension, with an Appendix on the Parachors of Mixtures.*

By THOMAS MARTIN LOWRY and GILBERT JESSOP.

THE experiments described below were undertaken with the idea that measurements of density and surface tension, followed by calculations of values of the parachor, might afford a sensitive method for the detection of sulphur tetrachloride, in view of the

regular way in which "pervalent" compounds, such as  $\text{PCl}_5$ ,  $\text{POCl}_3$ ,  $\text{SOCl}_2$ , etc., exhibit a deficiency of about 26 units as compared with the values deduced from compounds of normal valency. From this point of view, the results were once more negative, since the densities, surface tensions, and parachors all provided evidence of the presence of the dichloride, without giving any indication of the presence of the tetrachloride. Interesting results were obtained, however, by comparing the parachor values of mixtures of sulphur monochloride and chlorine before and after chemical combination had taken place.

#### EXPERIMENTAL.

*Density.—Methods.* Since the sulphur chlorides are decomposed by moisture, and may have a vapour pressure as high as 6 atm. at room temperature, the densities were determined by flotation in sealed tubes. Silica floats were used, partly because the densities of glass floats were altered when the liquid in which they were suspended was heated to bring it to equilibrium, and partly because their small coefficient of expansion was an additional advantage. The floats were hollow, about 15 mm. long and of 3 mm. diameter. A series, ranging from 1.42 to 1.76 at intervals of 0.02, was made, the desired density being attained first by adjusting approximately the amount of silica in the solid tip of the float, and then by grinding the tip and rounding it off in the oxyhydrogen flame. They were calibrated in mixtures of bromoform and toluene, the densities of which were measured with a pycnometer with vertical arms, specially designed to avoid loss by creeping after adjustment.

The samples of sulphur chloride were sealed up in thick-walled tubes, about 12 mm. in bore and 15 cm. long, together with two or three floats of suitable densities and the capillaries for measurements of surface tension, and were heated to  $100^\circ$  to bring about a condition of equilibrium. The tube was then clamped upright in a large water-bath, the temperature of which was maintained for 10 minutes within  $0.02^\circ$  of the temperature of flotation of each float, since a difference of  $0.01^\circ$  was sufficient to make a float rise or sink slowly.

*Results.* The densities of 35 samples, of chlorine contents ranging from 36.9 to 100 atoms %, were measured at two or three temperatures by the method just described. The coefficients of expansion were then calculated and the densities at  $15^\circ$  and  $0^\circ$  were deduced. Measurements were also made of four mixtures of sulphur monochloride and chlorine, which had not yet interacted to form the red dichloride and were therefore still pale yellow. The results are given in Table I.

TABLE I.

 (a) *Densities of equilibrium mixtures.*

At. % Cl.	Temp.	$d_4^{15}$ .	$d_4^{15}$ .	$d_4^{15}$ .	At. vol.† at 15°.
36.90	28.25°	1.72191	1.7389	1.758	
	33.40	1.72191*			
42.03	13.3	1.72191	1.71942	1.74140	
	-1.05	1.74294			
	18.3	1.72191*			
	3.8	1.74294*			
43.68	18.5	1.70780	1.71285	1.73449	
	8.72	1.72191			
	21.50	1.70780*	1.71718	1.73882	
45.30	12.90	1.70780*	1.70465	1.7272	
45.60	15.70	1.70780*	1.70895	1.73158	
	30.26	1.68592*			
48.50	5.18	1.70780	1.6928	1.7156	
50.0	15.98	1.68592	1.68744		20.01
50.0	1.8	1.70780	1.68721	1.71064	20.01
	15.83	1.68592			
52.07	11.6	1.68592	1.68063		20.14
54.34	6.92	1.68592	1.67264	1.69728	20.27
	21.78	1.66152			
58.20	-0.38	1.68592	1.65950	1.68532	20.51
	13.83	1.66152			
58.37	17.40	1.65578	1.66003		20.50
	24.85	1.64260			
59.73	-2.90	1.68592	1.65410	1.68080	20.60
	10.90	1.66152			
60.09	-3.60	1.68592	1.65286	1.67956	20.62
	10.20	1.66152			
61.87	17.60	1.64260	1.64725		20.74
	26.68	1.62638			
62.38	16.45	1.64260	1.64521		20.78
62.75	7.85	1.65578	1.64262		20.82
	15.10	1.64260			
64.28	4.85	1.65578	1.63685	1.66490	20.91
	11.92	1.64260			
66.13	17.93	1.62638	1.63192		
66.43	7.52	1.64260	1.62866	1.65662	21.08
	16.20	1.62638			
66.82	7.45	1.64260	1.62839	1.65668	21.08
	16.05	1.62638			
	23.00	1.61283			
67.04	-0.40	1.65578	1.62663	1.65502	21.11
	15.13	1.63638			
	22.11	1.61283			
69.23	16.16	1.61283	1.61543		21.30
	21.98	1.60128			
71.14	4.83	1.62638	1.60625		21.47
	11.68	1.61283			
73.31	0.58	1.62638		1.62755	
	7.30	1.61283			
74.16	9.25	1.60128	1.58926		21.75
	18.33	1.58230			
76.47	-1.45	1.61283		1.60988	
	4.22	1.60128			
81.20	17.62	1.54264	1.54856		22.49
	26.10	1.52351			
81.37	0.20	1.58230	1.55014	1.58273	22.47
	18.45	1.54264			

\* After heating.

† See p. 1011.

TABLE I (contd.).

(a) *Densities of equilibrium mixtures.*

At. % Cl.	Temp.	$d_4^{20}$	$d_4^{15}$	$d_4^{10}$	At. vol.† at 15°.
83.71	18.39	1.52351	1.53137		22.79
	28.60	1.49980			
90.05	2.15	1.52351	1.49249	1.52863	23.53
	12.09	1.49980			
	20.05	1.47977			
93.83	2.70	1.49980	1.46730	1.50693	24.02
	10.28	1.47977			
100	2.30	1.45980	1.42391	1.46630	24.90
	11.80	1.43296			
100	2.60	1.45980	1.4247	1.46715	24.89
100	2.62	1.45980	1.4247	1.46717	24.89

(b) *Mixtures of sulphur monochloride and chlorine.*

57.68	-5.0	1.63592	1.67714
	8.9	1.66152	
66.43	-0.80	1.64260	1.64404
	8.2	1.62638	
71.14	-3.95	1.62638	1.61933
	3.65	1.61283	
83.01	15.1	1.52351	1.5583

† See p. 1011.

The following data are added for comparison:

*Density of sulphur monochloride.*

	At 0°.	At 10°.	At 15°.	At 20°.
Popp (1855) .....	1.7055			
Hagen (1867) .....				1.6828
Thorpe .....	1.7094			
Trautz (1929) .....	1.709	1.6950		1.6790
Lowry and Jessop (1930) .....	1.7106		1.6872	

*Density of liquid chlorine.*

Marchand (1913) .....	1.468 at 0°; 1.434 at 12°.
Lowry and Jessop (1930) .....	1.4671 <sub>5</sub> at 0°; 1.4247 at 15°.

*Surface Tension.—Methods.* Since the measurements of surface tension had to be made in a sealed tube, the only method which could be used was that of capillary rise. On account of the difficulty of measuring accurately the position of the lower meniscus when using a single capillary tube, the double capillary method described by Sugden (J., 1921, 119, 1483) was finally adopted. Two capillaries, about 6 cm. long, with internal diameters of approx. 0.6 and 0.9 mm., were held together by glass bridges at the top and bottom. Glass projections were used in order to keep the capillaries upright and close to one side of the outer tube holding the liquid, so as to leave room for the silica floats which were also enclosed in the tube. Since the measurements were required primarily in order to calculate the parachor, which involves only the fourth root of the surface tension, no attempt was made to secure the



highest order of accuracy, nor was it considered necessary to procure capillaries which were accurately circular in cross section.

Calibration of the apparatus was carried out with benzene and checked with water, Sugden's values for the surface tension of these two liquids being used. The benzene was purified by fractional crystallisation and then distilled in an all-glass apparatus. The water was distilled from dilute permanganate in an all-glass apparatus, which had been thoroughly freed from grease, directly into the tube containing the capillary apparatus. The two calibrations agreed closely.

TABLE II.  
*Surface Tension and Parachor.*

(a) <i>Equilibrium mixtures.</i>					
At. % Cl.	Temp.	$\gamma^{\circ}$ .	$\gamma_0^{\circ}$ .	[ $P_{\Delta}$ ] calc. — [ $P_{\Delta}$ ] obs.*	
				for 100 atoms : $t^{\circ}$ .	$0^{\circ}$ .
50.0	16.3°	43.43	45.66	—7	7
52.07	20.2	41.6	—	2	—
54.34	15.0	40.48	42.70	33	39
58.20	17.1	38.10	40.61	47	53
58.37	18.2	38.18	—	39	—
59.73	14.6	37.70	39.79	53	64
60.09	15.2	37.56	39.75	52	61
61.87	15.7	36.84	—	49	—
64.28	—	—	37.63	—	69
66.82	15.0	34.39	—	58	—
67.04	14.5	32.24	36.58	53	59
69.23	20.1	31.87	—	65	—
73.31	—	—	33.03	—	80
74.16	16.0	29.47	32.53	83	69
76.47	—	—	30.84	—	99
81.20	19.0	24.91	—	99	—
81.37	—	—	28.20	—	103
83.71	13.0	24.81	26.81	94	98
90.05	15.9	21.79	24.31	75	81
93.83	16.4	20.44	23.31	44	44
100	12.9	18.87	21.10	2	5
100	—	—	21.21	—	—4
100	—	—	21.24	—	—3
(b) <i>Mixtures of monochloride and chlorine.</i>					
57.68	—	—	38.63	—	90
71.14	—	—	30.29	—	167
83.01	—	—	25.43	—	146

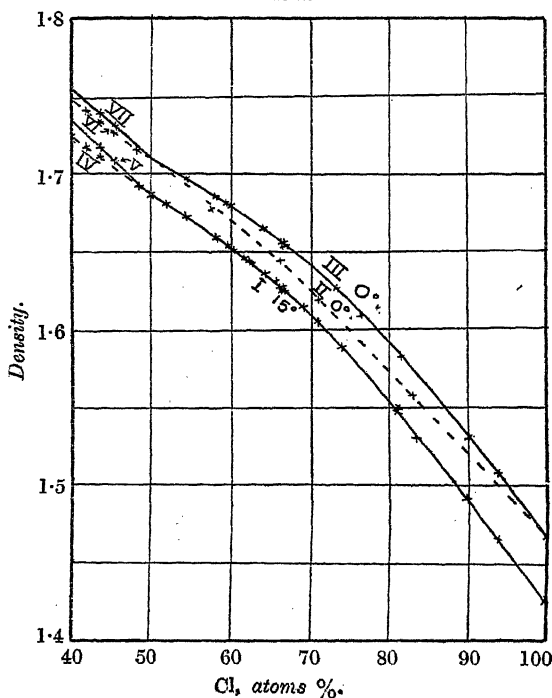
\* For definition of [ $P_{\Delta}$ ], see p. 1014.

If  $h$  is the difference in the heights of the liquid in the two tubes, measured from the base of one meniscus to the base of the other, and  $h_1$  and  $h_2$  are the respective heights of each meniscus, the corrected difference in rise,  $H$ , is given by  $H = h + \frac{1}{3}h_1 - \frac{1}{3}h_2$ , since Richards and Carver (*J. Amer. Chem. Soc.*, 1921, **43**, 827) found that  $\frac{1}{3}h$  is a sufficiently accurate meniscus correction for most purposes. If  $D$  is the density of the liquid, and  $d$  that of the

gas above the liquid, the surface tension is given by the equation  $\gamma = H(D - d)/k$ , where  $k$  is found from the calibrations. Values of  $d$  were estimated from the density of air together with Aten's values for the vapour pressure of sulphur chlorides of different compositions.

In making measurements of surface tension, the outer tube, with the apparatus enclosed, was clamped upright inside a small tank with a plate-glass front and back. It was illuminated from behind, through a water tank, to absorb heat rays, and a ground-

FIG. 1.



glass screen. The heights were read with a travelling microscope, reading to 0.001 mm. Comparative measurements on the same sample of liquid show a probable error of about 0.2 dyne per cm.

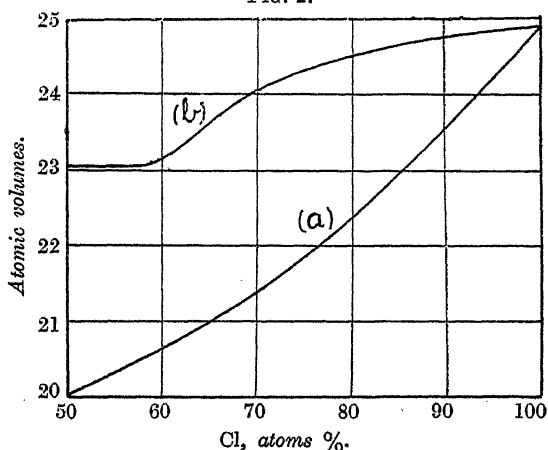
**Results.** The surface tensions, at room temperature or at 0° or both, of 23 equilibrium mixtures containing 50–100 atoms % of chlorine are set out in Table II, together with values for three mixtures of uncombined sulphur monochloride and chlorine.

Marchand (*J. Chim. physique*, 1913, 11, 574) gives for the surface tension of liquid chlorine the values 21.90 at 0° and 19.47 at 12.7°, as compared with our values, 21.22 at 0° and 18.87 at 12.9°.

### Discussion of Results.

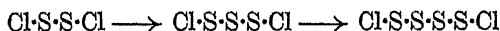
(a) The densities at 15° and at 0° of mixtures of sulphur monochloride and chlorine at equilibrium are plotted in Fig. 1, I and III. The curves are nearly linear from  $S_2Cl_2$  to  $SCl_2$ , after which the densities decrease more rapidly towards that of pure chlorine, but without giving any indication of a change of direction at the composition of the tetrachloride. The densities at 0° of uncombined mixtures of sulphur monochloride and chlorine, which are plotted in Curve II, are lower throughout, since chemical combination (which is revealed by a red coloration) is accompanied by a contraction, which reaches a maximum at or near the composition of the dichloride. Mixtures containing less than 50 atoms % of

FIG. 2.



(a) Mean atomic volumes. (b) Partial atomic volumes of chlorine.

chlorine also become more dense after being heated, as may be seen by comparing curves IV and VI (unheated) with V and VII (heated). This contraction is attributed to the formation of polysulphides:

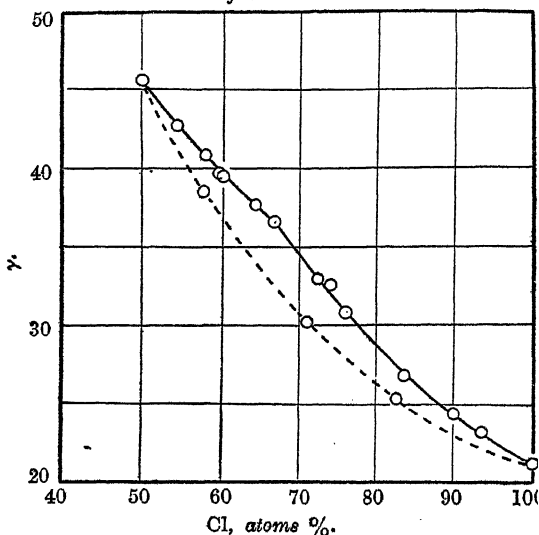


(compare Angeli and Magnani, *Gazzetta*, 1893, **23**, ii, 415; 1894, **24**, i, 349; Henrique, *Ber.*, 1894, **27**, 2993; Beckmann and Geib, *Z. anorg. Chem.*, 1906, **51**, 96; Bruni and Amadori, *Atti R. Accad. Lincei*, 1919, **28**, i, 217; Hammick and Zvegintzov, *J.*, 1928, 1785; Trautz, *Z. Elektrochem.*, 1929, **35**, 110).

An alternative way of displaying the densities is to plot the mean atomic volume,  $V = (A_1 n_1 + A_2 n_2)/d$ ; where  $A_1$  and  $A_2$  are the atomic weights, and  $n_1$  and  $n_2$  the atom fractions. The resulting curve for equilibrium mixtures at 15° (Fig. 2a) is at first nearly

linear, but rises more steeply as the composition of the dichloride is approached. A more sensitive method is to plot the partial atomic volume of the chlorine (Lewis and Randall, "Thermodynamics," New York, 1923), *i.e.*, the increase of volume when 1 g.-atom of chlorine is added to an infinite volume of the mixture and brought to equilibrium. The resulting curve (Fig. 2*b*) is at first horizontal, since monochloride is converted quantitatively into dichloride with a constant increment of volume, the mixture behaving in this respect as an "ideal solution." The curve then rises steeply through the composition of the dichloride; this rise corresponds with the range of dissociation of the dichloride, at the

FIG. 3.  
*Surface tensions.*



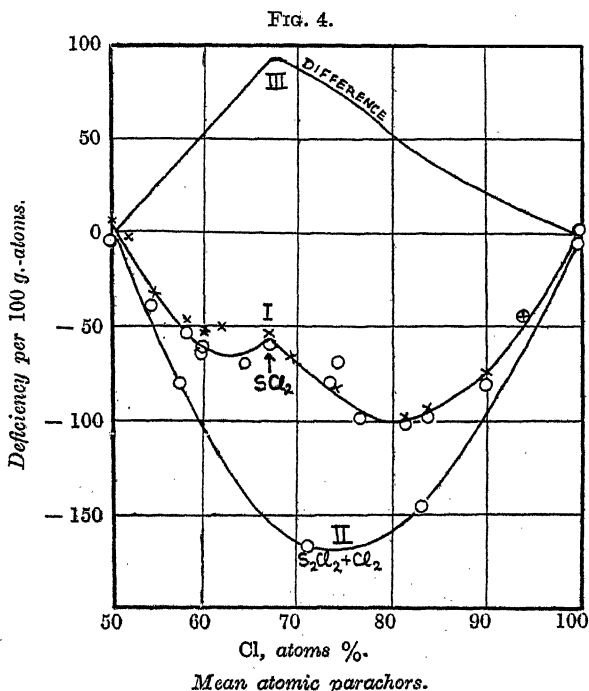
beginning of which the chlorine is all used to form dichloride whilst at the end it all remains free. Finally, the curve rises gently to the atomic volume of free chlorine, without any sign of discontinuity at the composition of the tetrachloride, although the slope of the line shows that the dichloride and chlorine do not form an ideal solution.

(*b*) The surface tensions, which are plotted in Fig. 3, increase progressively from 21.2 for chlorine to 45.7 for sulphur dichloride. The values for uncombined mixtures lie on a smooth curve; but those for equilibrium mixtures, which are higher throughout, cannot be represented by a simple curve. An attempt to represent the data by two curves unexpectedly revealed a discontinuity at

67 atoms % of chlorine, which is so close to the composition of the dichloride that the coincidence can scarcely be accidental. An even more striking discontinuity is seen in the "parachor deficiencies" (see below), but in neither case has any similar feature been observed at the composition of the tetrachloride.

### Summary.

1. The densities and surface tensions of equilibrium mixtures of the chlorides of sulphur have been measured from 37 to 100 atoms



% of chlorine, between  $-4^{\circ}$  and  $30^{\circ}$  and at  $0^{\circ}$  and room temperature respectively. The following constants have been determined:

	Densities.		Mol. volumes.		Surface tensions.	
	$0^{\circ}$ .	$15^{\circ}$ .	$0^{\circ}$ .	$15^{\circ}$ .	$0^{\circ}$ .	$15^{\circ}$ .
$S_2Cl_2$ .....	1.7106	1.6892	78.86	80.04	45.7	43.6
$SCl_2$ (equilm.) .....	1.6567	1.6285	62.10	63.2	36.6	34.4
$Cl_2$ .....	1.4671	1.4247	48.33	49.78	21.2	—

Well-marked discontinuities occur at the composition of the dichloride, but not of the tetrachloride. The densities and surface tensions of uncombined mixtures are lower than after combination has taken place.

2. The values found for the molecular parachors, *viz.*,  $\text{Cl}_2 = 104.6$ ,  $\text{S}_2\text{Cl}_2 = 205.5$ , lead to atomic parachors  $\text{S} = 50.48$ ,  $\text{Cl} = 52.28$ . The mean atomic parachors of intermediate mixtures are lower than those required by a linear law of mixing, but the deficiencies are smaller after combination (see Fig. 4 and Appendix). The single loop from  $\text{S}_2\text{Cl}_2$  to  $\text{Cl}_2$  is then replaced by a double loop from  $\text{S}_2\text{Cl}_2$  to  $\text{SCl}_2$  and from  $\text{SCl}_2$  to  $\text{Cl}_2$ , but with no indications of a break at  $\text{SCl}_4$ .

## APPENDIX.

*The Parachor of Mixtures.*—Hammick and Andrew (J., 1929, 754) recorded the existence of deviations from a linear relation in the parachors of mixtures, and suggested "that the deviation is connected with the Gibbs surface-adsorption effect," since it appeared to be associated with a *difference* in surface tension between the two components. Our experiments (which were completed nearly two years before, but had been circulated only in the form of a thesis) had already established the existence of similar deviations from the linear law, not only in mixtures of sulphur monochloride and chlorine, but also in mixtures of partly dissociated sulphur dichloride with sulphur monochloride and with chlorine; but, since the parachor is fundamentally a volume relationship, we do not regard the difference in surface tensions, nor the Gibbs surface-adsorption effect, as the only factor in producing these deviations. Thus, apart from the relative inaccuracy of all measurements of surface tension, there is no obvious reason why small changes of volume, produced by mixing a pair of optically isomeric compounds, should be exactly balanced by changes in the fourth root of the surface tension.

The methods and formulæ of Hammick and Andrew imply a knowledge of molecular constitution which we did not possess in this case. Our analysis of the problem was therefore carried out with the help of the mean atomic parachor, which we define by the equation  $[P_A] = (A_1n_1 + A_2n_2)\gamma^{1/4}/(D - d)$ , where  $A_1, A_2, n_1$  and  $n_2$  have the same significance as before (p. 1011). If there were no change in the parachors of the components, either on admixture or on chemical combination, the value of this function would be  $[P_A] = P_1n_1 + P_2n_2$ , where  $P_1$  and  $P_2$  are the atomic parachors of the two elements *as deduced from the molecular parachors of the limiting components of the system*. Our measurements give for the molecular parachors,  $\text{S}_2\text{Cl}_2 = 205.5$ ,  $\text{Cl}_2 = 104.6$ , whence  $\text{S} = 50.5$ ,  $\text{Cl} = 52.3$ ; whereas Sugden (J., 1925, 127, 1533) gives  $\text{S}_2\text{Cl}_2 = 205.1$ , and deduces (J., 1924, 125, 1188)  $\text{Cl}_2 = 111.5$  from the data of Marchand (*loc. cit.*), finally adopting for the atomic parachors the values  $\text{S} = 48.2$ ,  $\text{Cl} = 54.2$ .

The *atomic parachor deficiencies* plotted in Fig. 4, I and II, represent the differences ( $\times 100$ ) between the values of  $[P_A]$  derived from the two preceding equations (i) for equilibrium mixtures and (ii) for uncombined mixtures of sulphur monochloride and chlorine. It is therefore possible for the first time to make a direct comparison of the deviations from the linear law which are produced by chemical and by physical interaction between the components, in liquids of identical composition. The uncombined mixtures show the largest deviations, rising to a maximum of about 3% at about 75 atoms % of chlorine. When chemical combination takes place, this deviation is reduced, *e.g.*, to about 1% at the composition of the dichloride; but secondary maxima are then developed in mixtures of this compound with the two components from which it was formed. The curve III, which shows the change in the mean atomic parachor on chemical combination, rises to a maximum at or near the composition of the dichloride, but shows no analogous singularity at the composition of the tetrachloride.

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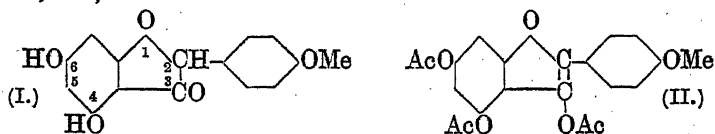
[Received, December 23rd, 1929.]

## CXXVI.—2-Arylcoumaranones.

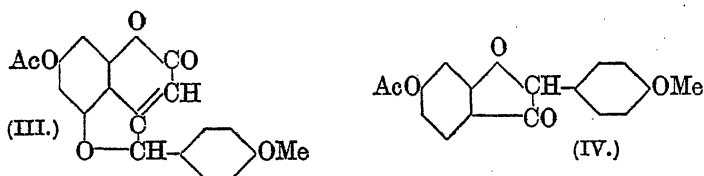
By WILSON BAKER.

AMONGST the methods available for the preparation of coumaranones are those in which a cyanohydrin or  $\alpha$ -monohalogeno-nitrile is condensed with polyhydric phenols under the conditions of the Hoesch synthesis (Sonn, *Ber.*, 1917, 50, 1262; Slater and Stephen, *J.*, 1920, 117, 309; Sonn and Falkenheim, *Ber.*, 1922, 55, 2975; Klarmann, *J. Amer. Chem. Soc.*, 1926, 48, 2366). Some years ago it was desired to synthesise 4 : 6-dihydroxy-2-p-methoxyphenylcoumaranone (I), since it appeared probable at one time that such a compound occurred naturally, and it was suggested to the author by Professor R. Robinson that such arylcoumaranones might be synthesised from the readily accessible *O*-benzoyl derivatives of aromatic aldehydes (Francis and Davis, *J.*, 1909, 95, 1404) by means of the Hoesch reaction. This expectation has been realised, but the yields are very poor and the products difficult to isolate except as acetyl derivatives. Further, the acetylation often takes an abnormal course. The use of aromatic aldehyde cyanohydrins themselves is prohibited owing to the ease with which they undergo condensation to derivatives of 1 : 4-diazines when treated with hydrogen chloride in ethereal solution (Minovici, *Ber.*, 1899, 32, 2206; Japp and Knox,

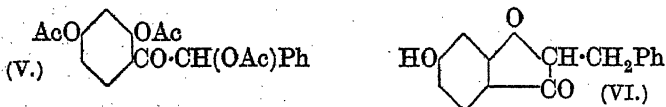
J., 1905, 87, 701; for mechanism of the reaction see Ingham, J., 1927, 694).



The interaction of *O*-benzoylanisaldehydecyanohydrin and phloroglucinol in ethereal solution with hydrogen chloride in presence of zinc chloride gave a solid ketimine, which after complete hydrolysis with concentrated hydrochloric acid yielded finally the coumaranone (I). Acetylation of the crude coumaranone with acetic anhydride and a trace of pyridine yielded 3 : 4 : 6-triacetoxy-2-*p*-methoxyphenylcoumarone (II) and *anhydro*-5-hydroxy-7-acetoxy-4- $\alpha$ -hydroxy-*p*-methoxybenzylcoumarin (III), which were separated by physical means. The constitution assigned to (III) is based on the facts that, unlike (I) and (II), it does not reduce Fehling's solution, and that its alcoholic solution has a violet fluorescence.



The analogous condensation of *O*-benzoylanisaldehydecyanohydrin and resorcinol gave, after complete hydrolysis, a product which could be obtained crystalline only after acetylation with acetic anhydride. This again proved to be a mixture, which was separated into 6-acetoxy-2-*p*-methoxyphenylcoumaranone (IV), and a compound of high molecular weight which did not reduce Fehling's solution and is tentatively regarded as 3-keto-6 : 3' : 6'-triacetoxy-2 : 2'-di-*p*-methoxyphenyl-2 : 3'-dicoumaranyl.



The condensation of *O*-benzoylbenzaldehydecyanohydrin with resorcinol yielded finally after acetylation 2 : 4-diacetoxy-*O*-acetylbenzoin (V), the ring in this case not having closed.

2-Arylcoumaranones of the type (I) could doubtless be prepared most readily by the condensation of  $\alpha$ -bromophenylacetonitriles with polyhydric phenols, and with this in mind  $\alpha$ -bromo- $\beta$ -phenylpropionitrile was condensed with resorcinol under the conditions of



the Hoesch reaction. Acid hydrolysis of the product gave a good yield of 6-hydroxy-2-benzylcoumaranone (VI), which on acetylation yielded 3:6-diacetoxy-2-benzylcoumarone. It is obvious that the condensation might proceed in a number of ways to give a compound  $C_{15}H_{12}O_3$ , which might be either (VI), 2:4-dihydroxyphenyl styryl ketone, 7-hydroxyflavanone, 7-hydroxy-4-phenyl-3:4-dihydrocoumarin (compare Fischer and Nouri, *Ber.*, 1917, 50, 611), or 7-hydroxy-3-benzylisocoumaranone. The physical properties of the reaction product are not in agreement with those of 2:4-dihydroxyphenyl styryl ketone (Ellison, J., 1927, 1720), and of the other possibilities only (VI) could give a diacetyl derivative.

Klarmann (*loc. cit.*) has condensed  $\alpha$ -bromo-*n*-butyronitrile with phloroglucinol by the Hoesch reaction and obtained a product which he describes as 4:6-dihydroxy-2-ethylcoumaranone. Although this reaction is exactly analogous to the case described above, and might lead to any of five isomeric products, no proof of the constitution of the substance was given; yet by analogy with the present case there can be little doubt that the compound isolated was actually the coumaranone.

The condensation of glycollonitrile with resorcinol has been described by Slater and Stephen (*loc. cit.*), who state that the reaction yields 6-hydroxycoumaranone. Karrer and Biedermann, however (*Helv. Chim. Acta*, 1927, 10, 441), find that the only product is  $\omega$ -hydroxyresacetophenone (fisetol). Full experimental details are not given by Slater and Stephen, but as the result of a number of experiments the author confirms the result of Karrer and Biedermann, and has further been unable to convert  $\omega$ -hydroxyresacetophenone into 6-hydroxycoumaranone by heating with various strengths of hydrochloric or sulphuric acid with or without the addition of zinc chloride—conditions which were probably used by Slater and Stephen in hydrolysing the ketimine.

#### EXPERIMENTAL.

*Condensation of O-Benzoylanisaldehydecyanohydrin with Phloroglucinol.*—(a) A solution of the cyanohydrin (30 g.; Francis and Davis, *loc. cit.*) and phloroglucinol (14.2 g.) in anhydrous ether (300 c.c.) was saturated with hydrogen chloride at room temperature. After 48 hours the solid ketimine was collected, washed with ether, and hydrolysed by heating with concentrated hydrochloric acid for 4 hours. The product was freed from benzoic acid by washing with sodium bicarbonate solution and was finally dissolved in alcohol (charcoal), and the solution concentrated to a small bulk. After several weeks the crystals which had separated from the viscous fluid were isolated by pressing the product between plates

of porous earthenware, and were then recrystallised from a very small volume of alcohol, being obtained in microscopic, almost colourless plates, m. p. 216—217° (Found: C, 66.2; H, 4.6.  $C_{15}H_{12}O_5$  requires C, 66.1; H, 4.4%). 4:6-Dihydroxy-2-p-methoxyphenylcoumaranone (I) gives a brownish-violet coloration with ferric chloride in alcoholic solution, and its solution in concentrated sulphuric acid is purplish-pink. It readily reduces Fehling's solution.

(b) A solution of the cyanohydrin (20 g.) and phloroglucinol (10 g.) in ether (200 c.c.) was saturated with hydrogen chloride, first at room temperature and then, after the addition of powdered anhydrous zinc chloride, at 0°. After 48 hours at 0°, water was added, and the ketimine hydrolysed by heating on the water-bath for 2 hours. The solid product was collected, heated for 1 hour in dilute sodium hydroxide solution, and reprecipitated by carbon dioxide. It was again collected, dried on porous earthenware, and acetylated by boiling with acetic anhydride and a trace of pyridine for 3 hours. The acetylated material was isolated by the addition of water and was obtained as light-brown crystals by recrystallisation from acetic acid (charcoal), in which it was sparingly soluble (yield, 7 g.). Three further crystallisations from acetic acid yielded a colourless product, which consisted of a mixture of compact prisms (A) and slender needles (B). An almost complete separation of the two substances was effected by stirring the mixture with alcohol, allowing the compact prisms to settle, and pouring off the alcohol while most of the thin needles were still suspended. The process was repeated several times, and finally both substances were separately crystallised from large volumes of alcohol.

Substance (A) separates from its hot alcoholic solution, which has a violet fluorescence, in thin, almost rectangular plates, m. p. 181—182° (Found: C, 67.4; H, 4.1.  $C_{19}H_{14}O_6$  requires C, 67.4; H, 4.1%). Anhydro-5-hydroxy-7-acetoxy-4- $\alpha$ -hydroxy-p-methoxybenzylcoumarin (III) gives a colourless solution in concentrated sulphuric acid, and does not reduce Fehling's solution.

Substance (B) separates from warm alcohol in very thin, prismatic needles, m. p. 174—175° (Found: C, 63.3; H, 4.6.  $C_{21}H_{18}O_8$  requires C, 63.3; H, 4.5%). 3:4:6-Triacetoxy-2-p-methoxyphenylcoumarone (II) gives a non-fluorescent solution in alcohol; the solution in concentrated sulphuric acid is a strawberry-red, which turns deep reddish-violet on standing. It readily reduces Fehling's solution.

*Condensation of O-Benzoylanisaldehydecyanohydrin with Resorcinol.*

—The condensation, and complete hydrolysis of the product, were carried out as in the case of the corresponding reaction with phloro-

glucinol (method b). The non-crystalline phenolic substance was acetylated by boiling with acetic anhydride for 6 hours, and the solid isolated by the addition of water was crystallised from acetic acid (charcoal) and then from alcohol, in the latter case the crystals being collected from the still warm solution. A further crystallisation from ethyl acetate gave small colourless needles, m. p.  $217^{\circ}$  (Found : C, 67.3; H, 5.2; *M*, by Rast's method, 646.  $C_{36}H_{30}O_{11}$  requires C, 67.7; H, 4.7%; *M*, 638). This substance gives a colourless non-fluorescent solution in alcohol; in concentrated sulphuric acid an orange solution is obtained, which slowly turns more pink. Prolonged hydrolysis with aqueous-alcoholic potassium hydroxide yields no benzoic acid, and the substance does not reduce Fehling's solution. It is most probably 3-keto-6:3':6'-triacetoxy-2:2'-di-*p*-methoxyphenyl-2:3'-dicoumaranyl.

The alcoholic mother-liquor from the crystallisation of the foregoing compound deposited minute slender needles, m. p. about  $135^{\circ}$ . This second substance was obtained, after two recrystallisations from alcohol, in colourless prismatic needles, m. p.  $139^{\circ}$  (Found : C, 68.4; H, 4.8.  $C_{17}H_{14}O_5$  requires C, 68.4; H, 4.7%). 6-Acetoxy-2-*p*-methoxyphenylcoumaranone (IV) readily reduces Fehling's solution and gives a colourless solution in concentrated sulphuric acid.

*Condensation of O-Benzoylbenzaldehydecyanohydrin and Resorcinol.*—A solution of the cyanohydrin (20 g.) and resorcinol (20 g.) in ether (150 c.c.) was saturated with hydrogen chloride at  $0^{\circ}$ , and powdered anhydrous zinc chloride added. After 24 hours water was added and the whole heated on the water-bath for 2 hours. The semi-solid product was dissolved in sodium hydroxide solution, reprecipitated with carbon dioxide, collected, and acetylated by boiling with acetic anhydride. The acetyl derivative isolated by the addition of water crystallised from alcohol in colourless prismatic needles, m. p.  $158^{\circ}$  (Found : C, 65.1; H, 4.5.  $C_{20}H_{18}O_7$  requires C, 64.9; H, 4.8%). 2:4-Diacetoxy-O-acetylbenzoïn (V) readily reduces Fehling's solution and gives a pale yellow colour in concentrated sulphuric acid.

*Condensation of  $\alpha$ -Bromo- $\beta$ -phenylpropionitrile and Resorcinol.*—A solution of  $\alpha$ -bromo- $\beta$ -phenylpropionitrile (10 g.; Baker and Lapworth, J., 1924, 125, 2333) and resorcinol (10 g.) in ether (100 c.c.) was saturated with hydrogen chloride at  $0^{\circ}$ , after the addition of a little powdered zinc chloride. After 48 hours water was added and the ketimine hydrolysed by heating on the water-bath for 1 hour. The solid ketone was collected and dissolved in dilute aqueous sodium hydroxide, and the solution shaken with chloroform. The alkaline layer was acidified; the solid obtained crystallised from chloroform (charcoal) in colourless, thick, diamond-shaped plates, m. p.  $161^{\circ}$

(Found in material dried at  $140^{\circ}$ : C, 74.7; H, 5.3.  $C_{15}H_{12}O_3$  requires C, 75.0; H, 5.0%). 6-Hydroxy-2-benzylcoumaranone (VI) gives no coloration with ferric chloride in alcohol, and does not reduce Fehling's solution. Its solution in concentrated sulphuric acid is pale-yellow.

The diacetyl derivative was prepared by boiling the parent substance (2 g.) with acetic anhydride (20 c.c.) and anhydrous sodium acetate (2 g.) for 3 hours. 3:6-Diacetoxy-2-benzylcoumarone, isolated by the addition of water, crystallised from methyl alcohol (charcoal) in colourless prismatic needles, m. p.  $76^{\circ}$  (Found: C, 70.5; H, 4.9.  $C_{19}H_{16}O_5$  requires C, 70.4; H, 5.0%). A monoacetyl derivative,  $C_{17}H_{14}O_4$ , requires C, 72.3; H, 5.0%).

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## CXXVII.—Organic Derivatives of Silicon. Part XLII. cycloHexyl Derivatives of Silicane and Silicoethane.

By KEITH WILLIAM PALMER and FREDERIC STANLEY KIPPING.

As the only known compounds containing tervalent silicon atoms are octaphenylsilicotetrasilane (J., 1923, **123**, 2590) and octa-*p*-tolylsilicotetrasilane (Steele and Kipping, J., 1929, 2545), prepared from the dichlorides  $R_2SiCl_2$ , it seemed of interest to try to obtain aliphatic analogues of these substances, especially as, at the same time, several outstanding problems relating to certain very sparingly soluble products (J., 1924, **125**, 2291) might be elucidated. As, however, the simple dialkyl derivatives of silicon tetrachloride are not very easily isolated, it was thought that dicyclohexylsilicon dichloride would be a more suitable starting point for the attainment of the objects in view.

Silicon tetrachloride was therefore treated with an ethereal solution of magnesium cyclohexyl bromide (about  $2\frac{1}{2}$  mols.), and the crude product, isolated in the usual way, was submitted to distillation (35 mm.). Except for dicyclohexyl and an unexpectedly small yield of impure cyclohexylsilicon trichloride, hardly any volatile product was obtained; at a certain temperature the oil began to froth and quickly changed into a bulky yellow solid, which was neither Grignard compound nor magnesium salt, and during this transformation, cyclohexene, dicyclohexyl, and hydrogen chloride were formed.

The attempted distillation of the crude oil under 1—2 mm. gave practically the same results as under the higher pressure; some

trichloride and a very little impure *dicyclohexylsilicon* dichloride were found in the distillate, but most of the product remained as a brittle solid. It was evident that the results of the interaction of silicon tetrachloride and magnesium *cyclohexyl* bromide, or of the distillation of the *cyclohexyl* derivatives of silicon tetrachloride, must be entirely different from those observed in any previous study of alkyl or aryl derivatives of the tetrachloride.

It was then found that the crude distilled dichloride, and also the non-volatile products, contained compounds which gave hydrogen with alkali; during the original reaction, or the subsequent distillation, therefore, silicon atoms had become directly united.

From the volatile products, *cyclohexylsilicon* trichloride was isolated without difficulty; on hydrolysis it gave a non-crystalline material, which consisted of a mixture of at least three condensation products derived from the hydroxide  $C_6H_{11}\cdot Si(OH)_3$ . When dried over sulphuric acid, these different substances gave "*cyclohexylsiliconic acid*" having approximately the composition  $(C_6H_{11}\cdot SiO\cdot OH)_n$ , which was insoluble in all ordinary solvents but gave a soluble crystalline salt with sodium ethoxide; when heated at  $150^\circ$ , the acid underwent further condensation, giving a product having the composition of the "anhydride"  $[(C_6H_{11}\cdot SiO)_2O]_n$ . These results correspond closely with those obtained by Meads and Kipping in their study of the phenyl-, benzyl- and propyl-"siliconic acids" (J., 1914, **105**, 679; 1915, **107**, 459).

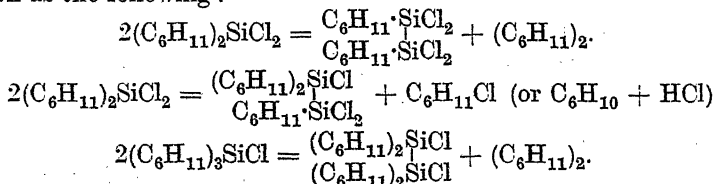
The dichloride  $(C_6H_{11})_2SiCl_2$  was not obtained free from *dicyclohexyl*; on hydrolysis it gave a non-crystalline solid, consisting of a mixture of condensation products of  $(C_6H_{11})_2Si(OH)_2$ , soluble in various organic solvents; when precipitated from its ethereal solution with glacial acetic acid, this substance melted at  $140$ – $145^\circ$ , but it underwent further condensation when kept or when heated at  $100^\circ$ , giving an anhydrous *dicyclohexylsilicanediol*  $[(C_6H_{11})_2SiO]_7$ . This final condensation product, therefore, is a mixture of compounds of the same order of complexity as those obtained from diethylsilicon dichloride (Martin and Kipping, J., 1909, **95**, 302), which gave an average molecular weight corresponding with  $[SiEt_2O]_7$ .

For the investigation of the non-volatile products of the original interaction, distillation was stopped just below that temperature at which frothing occurred; the residue was treated with ether, which precipitated an insoluble solid. The soluble matter from the ethereal solution gave on hydrolysis a mixture of at least two substances, one insoluble, the other soluble in ether. The former gave analytical data which corresponded with those required for a mixture of condensation products of the hydroxides  $C_6H_{11}\cdot Si(OH)_2$  and  $C_6H_{11}\cdot Si(OH)_3$ .

$\text{C}_6\text{H}_{11}\cdot\text{Si}(\text{OH})_2$ . The latter seemed to be a tetracyclohexylsilico-  
 $(\text{C}_6\text{H}_{11})_2\text{Si}\cdot\text{OH}$

ethanediol,  $(\text{C}_6\text{H}_{11})_2\text{Si}\cdot\text{OH}$ , which when heated at  $100^\circ$  was converted into a condensation product having a molecular weight of about 3000, corresponding with  $[(\text{C}_6\text{H}_{11})_4\text{Si}_2\text{O}]_7$ .

From these results it would seem that the interaction of silicon tetrachloride and magnesium cyclohexyl bromide takes place normally, giving cyclohexylsilicic trichloride, dicyclohexylsilicon dichloride and probably some tricyclohexylsilicic chloride. The yield of the dichloride, obtained by distillation, however, is very small and the main portion of the product which has been heated at  $150$ – $180^\circ$  consists of derivatives of silicoethane. Further, the quantity of dicyclohexyl obtained on distillation seems to be greater than that which could have been formed in the preparation of the Grignard reagent under the known conditions. It is inferred, therefore, that some of the original products of the reaction are converted at  $150$ – $180^\circ$  into derivatives of silicoethane by changes such as the following:



This inference is confirmed by the fact that the distilled mixture of dicyclohexyl and dicyclohexylsilicon dichloride gives, when heated, a solid residue similar to that referred to above. Further, since the crude product, before distillation, contains a small proportion of compounds in which silicon atoms are directly united, the formation of silicoethane derivatives occurs to some extent at or below  $100^\circ$ .

Many analyses of the solid produced during distillation have been made but without any definite results. This product contains only about 1 atom of chlorine to 4 silicon atoms and less than 1 cyclohexyl group to each silicon atom. From the hydrogen values of many samples it must be concluded that the elimination of hydrogen chloride and cyclohexene from the silicoethane derivatives is not accompanied by a further direct combination of silicon atoms, but rather by a fission of some of the  $\text{Si-Si}$  links. Its products of hydrolysis differ but little in composition from the original solid, and when treated with sodium hydroxide solution they give apparently sodium silicate and the sodium salt of "cyclohexylsilicic acid," without the production of any appreciable quantity of a fission product which is insoluble in aqueous alkali.

Until some other *cyclohexyl* derivatives of silicane have been studied, any suggestions as to the natures of these complex products would be of little value; it is hoped that work now in progress may afford some information.

#### EXPERIMENTAL.

*The Grignard Reagent.*—In the preparation of magnesium *cyclohexyl* bromide the yield is never theoretical; \* the best results (yield, 50–60%) were obtained as follows. Into a mixture of magnesium (18 g.) and ether (150 c.c.) containing a crystal of iodine, about 6 c.c. of a mixture of *cyclohexyl* bromide (120 g.) and ether (90 c.c.) are run. As soon as the initial vigorous reaction has somewhat subsided, the remainder of the bromide solution is added during 4–5 hours; the whole is then heated on a water-bath for  $\frac{1}{2}$  hour. Only about 5% of the magnesium remains undissolved and there is no deposition of magnesium salt.

*The Reaction with Silicon Tetrachloride.*—The solution of the Grignard compound ( $2\frac{1}{2}$  mols.) is dropped into an ice-cold, well-stirred solution of silicon tetrachloride (35 g.) in dry ether (50 c.c.). Magnesium halide begins to separate when about  $\frac{1}{3}$  of the reagent has been added, occasionally in the solid form, but more often as a brown or green oil, which in some cases does not crystallise even when, after the addition of all the Grignard reagent, the contents of the flask are heated on a water-bath under reflux during 3 hours. This oil, which passes through filter paper, contains about 60% of ether and probably consists of a saturated solution of ether in an etherate of magnesium chlorobromide of the class of compound described by Menshutkin (*J. Russ. Phys. Chem. Soc.*, 1907, **39**, 1548).

After having been heated until the deposition of magnesium salt seems to be at an end, the clear ethereal solution gives on evaporation a further quantity of magnesium salt as a purple crystalline mass, the yellowish liquid turning emerald-green; the latter is filtered, the residue washed with ether, and the combined filtrate and washings are again evaporated. These processes must be repeated three or four times before the solution ceases to give a deposit of magnesium halide. The liquid product, which is now light yellow, is submitted to distillation (35 mm.). At first a little *cyclohexene* passes over and then a considerable fraction is collected at 120–135°; this

\* Tschitschibabin (*Ber.*, 1905, **38**, 562) prepared the corresponding chloride in dry hydrogen, with a cooled reaction vessel, and used it to prepare esters, of which the yield was only 40%. Hell and Schaal (*Ber.*, 1907, **40**, 4162) observe that in the preparation of magnesium *cyclohexyl* bromide, the maximum yield of Grignard compound is about 60%; Adams and Noller ("Organic Syntheses," Vol. VI) give 61–65%.

contains *cyclohexylsilicon trichloride* and *cyclohexyl bromide*. The next fraction, collected up to  $150^{\circ}$ , consists almost entirely of *dicyclohexyl* but contains a little *dicyclohexylsilicon dichloride*. The temperature then rises rapidly to  $170$ – $180^{\circ}$  but only a very small quantity of liquid distils, and there is violent frothing, owing doubtless to the evolution of hydrogen chloride, with formation of a bulky solid. When the heating is discontinued, before frothing commences, while the whole contents of the flask are still liquid, the residue is soluble in dry ether with the exception of a small proportion of a yellowish solid, and the products in the ethereal solution, on hydrolysis, give a small proportion of the oxide  $[(C_6H_{11})_2SiO]_n$ , together with compounds containing linked silicon atoms. When, however, the heating is continued, the contents of the flask solidify, no dichloride distils, none can be extracted from the residue, and no diol is obtained by the hydrolysis of either the distillate or the residue.

When the crude product is distilled under 3–4 mm. pressure, the first fraction collected below  $120^{\circ}$  contains *dicyclohexyl* and *cyclohexylsilicon trichloride*; the next fraction, from  $140$ – $155^{\circ}$ , contains *dicyclohexyl* and *dicyclohexylsilicon dichloride*; a very small fraction passes over from  $155$ – $180^{\circ}$  and consists principally of the dichloride. At this stage the greenish, very viscous residue is almost entirely soluble in dry ether, but, if heating is continued, frothing occurs and the contents of the flask gradually become solid.

*cycloHexylsilicon Trichloride and "cycloHexylsiliconic Acid."*—The product collected from  $120$ – $135^{\circ}$  (35 mm.), fractionated at atmospheric pressure, afforded a colourless fuming liquid, b. p.  $208$ – $211^{\circ}$  (Found : Cl, 48.6.  $C_6H_{11}Cl_3Si$  requires Cl, 48.9%).

When this *trichloride* is dropped into well-stirred ice-cold water, a white solid is formed, but a considerable proportion of the hydrolysis product remains in solution, and only a small fraction of this dissolved matter can be extracted with ether. The solid, insoluble in water, when freshly precipitated is partly soluble in ether, and the ethereal solution on evaporation gives a colourless glue-like mass which rapidly hardens to a resin and becomes insoluble in ether. The original solid left at the ordinary temperature also becomes wholly insoluble in ether and other solvents; further, it is no longer completely soluble in cold sodium hydroxide solution. The aqueous solution of the original product of hydrolysis gives on evaporation a gelatinous precipitate which dries in the air to a white powder insoluble in water and in ether. Three samples of the preparation insoluble in water and in ether, dried over sulphuric acid during 24 hours and then for an hour at  $100^{\circ}$ , gave Si = 19.2, 19.0, and 19.0 (Calc. for  $C_6H_{11}SiO \cdot OH$  : Si, 19.4%).



Two such samples were heated first at 100° during 24 hours and then at 150° during 24 hours until constant in weight; the average loss (6.1%) corresponded with that (6.2%) required for  $2C_6H_{11} \cdot SiO \cdot OH = (C_6H_{11} \cdot SiO)_2O + H_2O$  and the heated products gave Si, 20.9 and 20.8 respectively [Calc. for  $(C_6H_{11} \cdot SiO)_2O$ : Si, 20.7%].

"*cycloHexylsiliconic acid*" dissolves slowly in warm 5–10% sodium hydroxide solution, from which it is immediately precipitated at the ordinary temperature or at 0° by ammonium chloride, but only after some time by dilute hydrochloric acid; only a very small proportion of this precipitate is soluble in ether and this rapidly becomes insoluble when it is kept. The insoluble form of the acid does not melt, but chars at a high temperature. When a solution of the sodium salt in 5% caustic soda is boiled, a slight odour of *cyclohexane* can be detected but decomposition is very slow as in the case of other alkylsiliconic acids (Meads and Kipping, J., 1914, 105, 688). With more concentrated solutions decomposition takes place more rapidly; after having been refluxed during 1 hour the products, precipitated by ammonium chloride and dried at 180–200°, gave the following results: From 8% NaOH, Si = 26.5; 20% NaOH, Si = 30.1; 30% NaOH, Si = 39.1; 40% NaOH, Si = 45.1 [ $(C_6H_{11} \cdot SiO)_2O$  requires Si, 20.7%.  $SiO_2$  requires Si, 46.6%].

The slow evaporation over sulphuric acid of a solution of the acid in alcohol containing the theoretical quantity of sodium ethoxide gave crystals, some cubic, some having a hexagonal outline, which quickly deliquesced and decomposed on being exposed to the air, changing into small globules of a glue-like substance.

*Dicyclohexylsilicon Dichloride and Anhydrodicyclohexylsilicanediol*.—The quantity of *dichloride* in the two crude fractions 140–155° and 155–180° (p. 1024) was so small that the compound could not be isolated; a fraction collected from 140–145° after several distillations gave Cl = 23.9 [ $(C_6H_{11})_2SiCl_2$  requires Cl, 26.7%]. When a portion was heated (760 mm.), a little *dichloride* and *dicyclohexyl* distilled but as heating was continued most of the oil was converted into a glue-like mass, which finally changed to a bulky solid.

*Dicyclohexylsilicanediol* was obtained by hydrolysing the crude *dichloride* and then separating the *dicyclohexyl* by distillation in steam. It was more conveniently prepared by hydrolysing the oil which remains when distillation is stopped as soon as *trichloride* ceases to pass over. The pasty product, freed from *dicyclohexyl*, is a pale yellow, dough-like mass most of which dissolves in ether, leaving a pale yellow solid quite insoluble in that solvent. The latter gives hydrogen with caustic soda and is described later.

The ethereal solution is agitated with dilute caustic soda solution until hydrogen evolution ceases, washed with water, and evaporated; the pale glue-like residue when left in the air changes into a brittle resin, which softens at about  $200^{\circ}$ , gradually liquefies at higher temperatures, and then chars. When glacial acetic acid or alcohol is added to a cold ethereal solution of the glue-like substance, a white, apparently amorphous, granular solid is precipitated under certain conditions; this product melts indefinitely at  $145-150^{\circ}$  and, when left during about  $\frac{1}{2}$  hour in the acid solution, becomes a glue-like mass; when kept during a day or two, it changes into the resinous form, which decomposes at  $200-250^{\circ}$ .

The precipitated powder was dried in the air and at  $100^{\circ}$  until constant in weight; four different samples gave  $\text{Si} = 13.3; 13.0; 13.2; 13.4$  [Calc. for  $\{(\text{C}_6\text{H}_{11})_2\text{SiO}\}_n$  :  $\text{Si}$ , 13.3%]. Cryoscopic determinations gave (a) in benzene,  $M$ , 1438 and 1481; (b) in camphor,  $M$ , 1450 and 1460.

These results show that the simple diol is unstable; the physically different preparations mentioned above are doubtless mixtures of condensation products like those obtained from other diols and the fact that the average molecular weight is as high as 1455 points to the presence of very complex compounds corresponding with some of those obtained from diphenylsilicanediol (Kipping and Murray, *J.*, 1928, 1427).

*Derivatives of Silicoethane.*—The very viscous, dark green residue which is obtained when the distillation of the crude product is discontinued at about  $180^{\circ}$  is treated with dry ether, which precipitates a small quantity of yellowish solid. The filtered solution gives on evaporation a very thick oil, which when heated under reduced or atmospheric pressure is converted into a yellow solid with evolution of hydrogen chloride, giving a distillate consisting of *cyclohexene*, *dicyclohexyl*, and a small proportion of some compound which evolves hydrogen with aqueous alkalis; the crude oil was analysed (Found:  $\text{Cl}$ , 21.4%; 1 g. gave 52 c.c. of hydrogen. Two other preparations gave hydrogen values of 51.2 and 52.7 respectively). These results are considered later (p. 1028).

The oil hydrolysed with cold water gives a creamy mass which hardens to a crisp solid. A very variable quantity, sometimes as much as 40%, of this product is soluble in ether and the proportion seems to depend on the stage at which distillation has been stopped. The insoluble portion is a granular infusible powder insoluble in all the solvents which were tried. Three different preparations were dried at  $100^{\circ}$  and analysed (Found:  $\text{Si}$ , 19.0, 18.8, and 17.3% respectively). They all evolved hydrogen with caustic alkalis and gave respectively the following values: 70, 69, and 67.4 [Calc. for

$\text{C}_6\text{H}_{11}\cdot\text{SiO}$  : Si, 22%; hydrogen value 80. Calc. for  $\frac{\text{C}_6\text{H}_{11}\cdot\text{SiO}}{(\text{C}_6\text{H}_{11})_2\text{Si}\cdot\text{OH}}$  :  
 $\text{C}_6\text{H}_{11}\cdot\text{SiO}$  : Si, 16.9%; hydrogen value 66].

These results agree with the view that the ether-soluble residue from the distillation contains a mixture of di- and tri-*cyclohexyl* derivatives of silicon hexachloride and that this insoluble substance is a mixture of the condensation products formed when they are hydrolysed. The proportions of the two chlorides would no doubt depend on the temperature at which distillation had ceased and the composition of the mixed products of hydrolysis would vary accordingly.

That this insoluble product contains linked silicon atoms is proved by its behaviour towards alkalis; that it contains both  $\text{R}_2\text{Si}<$  and  $\text{RSi}\leq$  groups is proved by the fact that after fission has occurred the alkaline solution contains in suspension a glue-like substance, soluble in ether, which has all the (rather indefinite) properties of the oxide  $(\text{C}_6\text{H}_{11})_2\text{SiO}$ . The alkaline solution treated with acids gives a precipitate of "*cyclohexylsiliconic acid*."

The product of hydrolysis which is soluble in ether was obtained as a glue-like mass by the evaporation of the solution. It dissolved freely in ether but was less readily soluble in acetone, from which it separated again in a glue-like form. As it might have contained a small proportion of the oxide,  $(\text{C}_6\text{H}_{11})_2\text{SiO}$ , it was fractionally extracted with cold acetone, in which the latter is readily soluble, and then dried over sulphuric acid until constant in weight (sample I); the last acetone extract was evaporated and the residue dried in like manner (sample II) [Found: (I) Si, 13.2%; hydrogen value, 53. (II) Si, 12.4%; hydrogen value, 50. Calc. for  $(\text{C}_6\text{H}_{11})_4\text{Si}_2(\text{OH})_2$ : Si, 13.3%; hydrogen value, 53.5]. That the compound contains the group  $\text{SiR}_2$  was proved by the fact that, when it was treated with aqueous alkali until hydrogen ceased to be evolved, it did not dissolve but gave a product which behaved in all respects like the oxide and contained 12.1% of silicon (Calc. for  $\text{SiR}_2\text{O}$ : Si, 12.3%).

The less soluble portion (I) of this tetracyclohexyl derivative was dissolved in ether, and a little alcohol added to the solution. There was an immediate precipitate of a colourless infusible solid, which, dried over sulphuric acid until constant in weight, gave a hydrogen value of 56.5 and *M* (cryoscopic) in benzene 2980 and in camphor 2900. This product was still soluble in ether, acetone and other solvents, but it could not be obtained in crystals. These results indicate that 7 mols. of the dihydroxide have undergone condensation with the loss of 6 or 7 mols. of water to form

$\text{HO}\cdot\text{Si}_2\text{R}_4\cdot\text{O}[\text{Si}_2\text{R}_4\cdot\text{O}]_5\cdot\text{Si}_2\text{R}_4\cdot\text{OH}$   
 or the closed-chain compound  $[\text{Si}_2\text{R}_4\text{O}]_7$ .

The analytical data given above for the original oily residue (p. 1026) and the results of the investigation of its products of hydrolysis accord with the view that the oil consists principally of the two compounds  $\text{SiR}_2\text{Cl}\cdot\text{SiR}_2\text{Cl}$  and  $\text{SiR}_2\text{Cl}\cdot\text{SiRCl}_2$  with a very variable proportion of  $\text{SiRCl}_2\cdot\text{SiRCl}_2$ .

*The insoluble residue.* The yellow porous infusible solid which remains when the distillation of the crude original product is continued until liquid ceases to pass over, is not present in the original oil; during its formation, hydrogen chloride, cyclohexene and di-cyclohexyl are produced. As it was insoluble in all organic solvents which were tried, it was directly analysed, 6 different preparations being used. The percentage of silicon ranged from 22.9 to 25.5 and the hydrogen values from 45—52.5; a chlorine determination, in one sample only, gave  $\text{Cl} = 9.0\%$ . It is noteworthy that the hydrogen values are no greater than that of the oil from which it has been formed, in spite of the loss of halogen and hydrocarbon radicals.

When left in contact with aqueous alcohol during many hours and then washed, crushed and dried, the solid gave a cream-coloured powder, insoluble in all the common solvents. Several preparations were analysed, but, as was to be expected in view of the small proportion of halogen which was displaced by hydroxyl, the silicon percentages and the hydrogen values were practically the same as those of the non-hydrolysed solid. The only other evidence as to the nature of this product was obtained by warming the solid with acetone and sodium hydroxide until hydrogen ceased to be evolved; with the exception of a small and variable proportion of glue-like matter, the solid was thus converted into products soluble in aqueous alkali, and these were fractionally precipitated by passing carbon dioxide into the solution. The three precipitates thus obtained, when dried, contained 29.5, 22.3 and 19.8% of silicon respectively; since  $\text{C}_6\text{H}_{11}\cdot\text{SiO}\cdot\text{OH}$  requires Si, 19.4% and the sodium hydroxide solution was not sufficiently strong to decompose the silicic acid, it must be concluded that some of the silicon atoms in the solid are not combined with cyclohexyl groups.

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CXXVIII.—*Organic Derivatives of Silicon. Part XLIII. The Formation of Tri- and Tetra-phenylsilicane by the Action of Sodium on Triphenylsilyl Chloride.*

By FREDERIC STANLEY KIPPING and JOHN FRANCIS SHORT. ]

THE action of sodium on phenylsilicon trichloride in boiling xylene solution in an atmosphere of nitrogen results in the production of a very complex mixture, the soluble components of which contain from 6 to 50 atoms of silicon in their molecules; some of these components, submitted to fission with alkalis, give diphenylsilicanediol and therefore contain  $>\text{SiPh}_2$  groups (Kipping, Murray, and Maltby, J., 1929, 1180). In the absence of a solvent in the presence of dry air the trichloride is almost entirely converted at about  $180^\circ$  into a product which is insoluble in all ordinary solvents; but in the absence of air the reaction seemed to proceed differently (*loc. cit.*, footnote, p. 1184).

In the course of further experiments in which the trichloride was heated with the metal in a stream of pure nitrogen, tri- and tetraphenylsilicane were obtained.

The formation of the last-named compound is probably due to the prior production of sodium phenyl, which then reacts with the unchanged trichloride; the same suggestion was made to account for the presence of  $>\text{SiPh}_2$  groups in some of the compounds obtained in xylene solution (*loc. cit.*, p. 1183). The related observations on the formation of tri- and tetra-benzyl derivatives from dibenzylsilicon dichloride and sodium (Steele and Kipping, J., 1928, 1431) seem to show that aryl groups generally, directly combined with silicon, may give sodium aryl compounds; the alternative view that aryl chloride separates and then reacts with the unchanged silicon halide in the presence of sodium seems to be less probable; but, however produced, the unexpected formation of tetraphenylsilicane in this and other reactions (Kipping and Murray, J., 1929, 360) affords an interesting contrast to the non-formation of tetraphenylmethane under conditions which might be expected to give it.

The production of triphenylsilicane from the trichloride is difficult to explain. It was at first thought that the hydrogen in this compound might be derived from sodium hydride, which is present in the metal in very small proportion; but when the trichloride is heated at its boiling point with sodium hydride in the absence of air during many hours there is no sign of any reaction. As it also seems impossible that the hydrogen can be derived from any phenyl-

ethoxysilicon dichloride present in the purified trichloride (J., 1929, 1184), it is necessary to assume that it is formed from phenyl groups by changes such as  $2 >\text{SiPh}_2 \rightarrow >\text{SiPh}\cdot\text{C}_6\text{H}_4\cdot\text{SiPh}_2 + \text{H}$ . This assumption was made in order to account for the production of triphenylsilicane from octaphenylcyclosilicotetrane (Kipping and Murray, *loc. cit.*) and considering the high temperature at which that change occurred it seemed to be a reasonable one; there was also some collateral evidence of the presence of phenylene groups in some of the products. In the experiments with the trichloride the temperature hardly exceeds  $200^\circ$ , unless locally, and such an explanation of the origin of the hydrogen is less probable, but there seems to be no alternative.

The yields of the tri- and tetra-phenyl derivatives cannot be given exactly; they both seem, however, to be less than 3% of the weight of the chloride.

#### EXPERIMENTAL.

To freshly distilled phenylsilicon trichloride (10—15 g.) contained in a 400 c.c. flask, large clean blocks of sodium ( $4-4\frac{1}{2}$  atoms) are added and a stream of oxygen-free nitrogen, dried finally with phosphoric oxide and sodium wire, is passed through the apparatus, which is provided with an upright quill-tube air-condenser about 30" long. The escaping gas is led through two wash-bottles containing benzene (or xylene) and after passing a mercury seal is bubbled through water. When all the air has been expelled, the flask is heated in an oil-bath and the nitrogen stream is reduced to about 1 bubble per second. Just below the boiling point of the trichloride the bright metal becomes coated with a brown crust and appears to increase considerably in volume. Gentle agitation releases the molten metal, which then becomes encrusted as before, and in the course of an hour or so a film of oil is usually visible in the condenser; the heating at about  $190^\circ$  is continued until the contents of the flask have become almost solid (about 10—20 hours). In some experiments, in which the temperature was finally raised to about  $230^\circ$ , crystals of tetraphenylsilicane were deposited on the upper portions of the flask and drops of oil, collected from the lower end of the air-condenser, were found to consist almost entirely of triphenylsilicane. If the flask is very vigorously shaken when the reaction has well started and the temperature has risen to about  $160^\circ$ , a great development of heat occurs and the contents of the flask are rapidly transformed into a granular brown solid.

In an experiment in which sublimed sodium hydride was used instead of sodium there was no sign of any reaction and the surface of the hydride was not coated with any crust even when the contents of the flask had been gently boiled during some 8—10 hours.

The oily film which, when sodium was used, coated the whole length of the condenser, and in which six-sided prisms were sometimes detected, was readily soluble in cold acetone, most of the crystalline matter being undissolved; this solution was practically free from chlorine and on evaporation yielded about 0.2 g. of a colourless viscous residue which did not crystallise at 0°. This product had the properties of triphenylsilicane (J., 1929, 364); when treated with aqueous alkali and a little acetone, it was rapidly attacked at the ordinary temperature with the evolution of hydrogen and formation of triphenylsilicol. The latter was fully identified by converting it into triphenylsilicyl oxide and crystallising the product from benzene; the highly characteristic rhomboidal crystals, *m. p.* 222°, of the oxide, which became opaque at 100°, were obtained. Small additional quantities of crude triphenylsilicane may be extracted from the main product with light petroleum (*b. p.* 30–40°).

The crystals sparingly soluble in acetone from the air-condenser and those forming a sublimate in the reaction flask were recrystallised from boiling acetone; the product, usually less than 0.1 g., was thus obtained in highly lustrous needles which were proved to be those of tetraphenylsilicane by direct comparison and by mixed melting-point determinations.

The products which were collected in the benzene wash-bottle are still under investigation; it seems that they contain either silicochloroform or silicon dichloride; and the water with which the escaping nitrogen was finally washed contains hydrochloric acid.

The main product of the reaction has not been thoroughly investigated, as it is no doubt a very complex mixture similar to that formed from the trichloride in boiling xylene solution; further, it is very difficult to decompose completely all the silicon halide and after 15–20 hours' heating the mixture still contains halogen compounds soluble in benzene which would make its investigation even more troublesome than that of the halogen-free products previously described. In order, however, to try to ascertain the approximate yield of the tetraphenyl derivative the products soluble in cold benzene were fractionally crystallised from that solvent and then from acetone; most of the fractions thus obtained were glue-like in consistency, but some of the more soluble portions seemed to be partly crystalline and from these after many operations there was isolated about 0.2 g. of crystalline matter. This product melted at 229–230° and gave with pure silicon tetraphenyl a mixture which melted from 230–232°, but it separated from solvents, including acetone, in microscopic nodules, whereas tetraphenylsilicane always crystallises from that solvent in highly lustrous needles; when warmed with acetone and aqueous alkali, it gave a little hydrogen

and therefore contained some linked silicon atoms, but after this impurity had been eliminated almost the whole of the substance was recovered apparently unchanged in crystalline form and in melting point. Since it had been found that tetraphenylsilicane sublimed readily, this nodular material was heated at about 220°; pure tetraphenylsilicane sublimed in lustrous needles, leaving only a very small proportion of gelatinous matter. Several of the more soluble fractions of the main products were treated with acetone and aqueous alkali until the hydrogen evolution ceased and after evaporation of the acetone the insoluble matter was again fractionated, but only very small quantities of tetraphenylsilicane were thus obtained. It seems, therefore, that the total yield of this compound is not very much greater than that of the triphenyl derivative.

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### CXXIX.—*The Mechanism of, and Constitutional Factors controlling, the Hydrolysis of Carboxylic Esters. Part I. The Constitutional Significance of Hydrolytic Stability Maxima.*

By CHRISTOPHER KELK INGOLD.

ALTHOUGH the mass of data, accumulated by Victor Meyer, Kellas, Sudborough, Reid, and others, relating to the rates of hydrolysis of carboxylic esters and amides, forms one of the main pillars of the theory of steric inhibition, an examination of the results reveals the existence of a large number of anomalies of which no explanation has yet been given. The point may be exemplified by reference to the acid hydrolysis of two simple series, one of ethyl esters (Löwenherz, *Z. physikal. Chem.*, 1894, **15**, 388), and the other of acetates (Palomaa, *Ann. Acad. Sci. Fennicæ*, 1913, *A*, **4**, 2; 5, 4; Skrabal and Hügetz, *Monatsh.*, 1926, **47**, 17; and others), for which the data\* fail to show the continuous gradations which might have been expected.

	$k \times 10^3$ (40°).		$k \times 10^3$ (25°).
Ethyl acetate .....	26.2 min. <sup>-1</sup>	Methyl acetate .....	6.8 min. <sup>-1</sup>
„ chloroacetate ...	15.2 „	Ethyl acetate .....	6.6 „
„ dichloroacetate	24.4 „	isoPropyl acetate .....	3.6 „
		tert.-Butyl acetate .....	7.5 „

On the other hand, it has recently been proved that the hydrolysis of carboxylic esters is just as susceptible to polar influence as are

\* It will be the uniform practice in these papers to employ minutes as time units and to use  $\log_e$ , not  $\log_{10}$ , in integration formulæ for velocity coefficients. Data from the literature are corrected, where necessary, to conform with these conventions.



most other reactions. Probably the clearest demonstration of this is to be found in the circumstance that Kindler's results (*Annalen*, 1926, 450, 1) for the speed of hydrolysis of benzoic esters containing various substituents in the *m*- and *p*-positions are in excellent agreement with the purely electropolar scheme which has been evolved (Ingold, *Ann. Reports*, 1927, 24, 155; 1928, 25, 146; Ingold and Rothstein, J., 1928, 1217; compare Williams, this vol., p. 37) for the interpretation of the influence of *m*- and *p*-nuclear substitution on aromatic side-chain reactions generally. In such a group of examples, complication is at a minimum: the electronic conductivity of the benzene ring guarantees the facile transmission of polar influences, whilst its configuration and spatial rigidity render steric inhibition practically inoperative. The clear implication, however, is that in the general case of ester hydrolysis, in which spatial effects are obviously of importance, internal polar factors will also play a part, and that this may explain the anomalies illustrated.

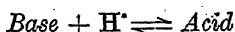
The theoretical object contemplated in this series of communications is the development of methods for the separation of the two factors presumed to be present in general on the basis of the arguments indicted. An analogy for the procedure adopted is provided by a contemporaneous investigation (Gane and Ingold, J., 1929, 1691; and earlier) in which a similar problem is envisaged, *viz.*, the separation of the spatial and internal polar factors which together control the strengths of polybasic acids. Here the analysis was greatly facilitated by the consideration, in the first instance, not of the dissociation constants themselves, but of a function of them, presumed, on the basis of an approximate theory, to be related mainly to *one* of the operating factors.

The development of an analogous procedure for the hydrolysis of esters necessitates some consideration of the theory of the dynamics of homogeneous catalysis as it has been elaborated by Brönsted and Dawson especially. It may be stated that our investigation is based on—indeed, was rendered possible by—Dawson's elegant methods for the analysis of superimposed catalytic effects; and, further, that due consideration has of necessity been given to certain highly important points raised by Brönsted in the course of his work.

The Arrhenius-Ostwald theory of catalysis by hydrogen and hydroxyl ions (symbolised,  $v = v_H + v_{OH}$ ) has more recently been extended, in several well-defined stages, to include catalysis by a large variety of molecules and ions. The "dual" theory of catalysis ( $v = v_H + v_{OH} + v_m$ ) envisaged catalysis by the undissociated molecules of acids (Acree and Johnson, *Amer. Chem. J.*, 1907, 37, 410; 38, 258; Senter, J., 1907, 91, 460; Lapworth, 1910,

97, 19; Goldschmidt and Thuesen, *Z. physikal. Chem.*, 1910, 70, 627; 1912, 84, 30; *Z. Elektrochem.*, 1911, 17, 684; Bredig, Miller, and Braune, *ibid.*, 1912, 18, 535; Snethlage, *ibid.*, p. 539; Taylor, *ibid.*, 1914, 20, 201; Dawson, Powis, and Reiman, J., 1913, 103, 2135; 1915, 107, 1426), and the most important step in its super-session by a still more general theory ( $v = v_H + v_{OH} + v_m + v_a$ ) consisted in the recognition of catalysis by the anions of acids (Brönsted, Pedersen, and Drus, *Z. physikal. Chem.*, 1924, 108, 185; 1925, 117, 299; Dawson and Carter, J., 1926, 2282). Many claims have been made for the recognition of a small but distinct catalytic effect of the water molecule on reactions in aqueous solution, but few are substantial ( $v = v_H + v_{OH} + v_m + v_a + v_{H_2O}$ ); the established cases include the mutarotation of glucose (Hudson, *J. Amer. Chem. Soc.*, 1907, 29, 1571; Brönsted and Guggenheim, *ibid.*, 1927, 49, 2554) and the iodination of acetone (Dawson and Key, J., 1928, 543).

Brönsted and Guggenheim discussed their results on the mutarotation of glucose in relation to the conception in accordance with which acids and bases are defined by the equation



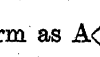
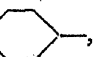

{e.g.,  $[\text{Co}(\text{NH}_3)_5\text{OH}]^{2+}, \text{NH}_3, \text{OH}^-$ } {e.g.,  $\text{NH}_4^+, \text{H}^+, \text{CO}_2\text{H}, [\text{CO}_2\text{CO}_2\text{H}]^-$ },

independently of their state of electrification. (In this scheme  $\text{OH}^-$  appears as a special instance of a base, and the hydron,  $\text{H}_3\text{O}^+$ , as a special case of an acid; water is remarkable as belonging to both categories.) They showed that the catalytic efficiencies of a series of bases (including  $\text{OH}^-$ ) increased with the strength of the base, and that the logarithmic plot of the catalytic coefficients against the equilibrium constants of the reaction formulated above approximated to a straight line having a certain slope. Similarly, the catalytic effects of a series of acids (including  $\text{H}_3\text{O}^+$ ) increased with the strength of the acid, and an analogous plot of the data yielded another straight line of different slope. Evidently there are two catalytic mechanisms corresponding to the two lines: in acid catalysis the reactant receives from the catalyst a positive charge, and in basic catalysis it confers on the catalyst a positive charge. These conditions are fulfilled by both Lowry's (J., 1925, 127, 1371) and Baker's (J., 1928, 1583) theories of catalytic effects on mutarotation in the sugar series, but the general conclusion must hold independently of the accuracy of the assumed mechanistic details; and it is clear, moreover, that the actual mechanism of catalysis by hydrons is also that of catalysis by acids, and that the mechanism of catalysis by hydroxyl ions applies equally to catalysis by bases, in the generalised interpretation of the terms acid and base. Again, since the coefficients representing the catalytic

activities of ten acids and five bases on the iodination of acetone (Dawson and others, J., 1926, 2282; 1928, 543, 2844; 1929, 1884, 2530) yield a closely similar bilinear plot, it can be claimed that there is experimental evidence for extending the same two mechanisms, with their distinctive electropolar characteristics, to prototropic change generally, for it is usually accepted that the prototropy of acetone is here involved. Furthermore, Dawson and Lowson's results (J., 1927, 2107; 1928, 2152; 1929, 393, 1229) for the effect of three acids and two bases on the hydrolysis of ethyl acetate adumbrate yet another diagram of the same type, so that the principle of a dualistic mechanism of polar catalysis in relation to the generalised conception of acids and bases may evidently be extended to the hydrolysis of carboxylic esters. It should be stated that Lowry (*loc. cit.*), on theoretical grounds, suggested a close relation between the catalysis of sugar mutarotation and that of ester hydrolysis. Probably a still wider generalisation would be justifiable.

The explicit discussion will now be confined to catalysis by hydrogen and hydroxyl ions in ester hydrolysis, the implication being that the statements made are applicable to acid and basic catalysis generally, except in so far as quantitative modification is necessitated by the specific nature of an acid or base.

Consider the  $n$ th ester of an isotypic series. (We cannot yet define the word "isotypic," which is inserted to retain the right to exclude certain cases: the theory here advanced is an approximate one, and whilst the comparison to be instituted *might* embrace all carboxylic esters, except, perhaps, a few special classes such as lactones or 1:1-alkylidene di-esters, it might, on the other hand, prove to be much more restricted.) First, the formula of the series may be taken as  $R \cdot CO \cdot OR'$  in which  $R$  is variable and  $R'$  constant. Let  $k_H$  and  $k_{OH}$  be the catalytic coefficients expressing the rates of hydrolysis of the typical member at a given temperature by hydrogen and hydroxyl ions respectively. Now, it is possible to suppose that the *polar* effect of the variable group  $R$  on the constant residue  $\cdot CO \cdot OR'$  is capable of being quantitatively *imitated* by a group  $G$  of such a form that, when  $R$  is varied, the variations of  $G$  necessary to preserve the imitation do not alter the *steric* value of  $G$  in relation to the residue  $\cdot CO \cdot OR'$ . (For example,

$G$  might be of such a form as  $A$  ,  $A$  , or  $A$  , where  $A$  is variable, and  $B$  constant.) Let

$k_H^G$  and  $k_{OH}^G$  be the corresponding catalytic coefficients for the hydrolysis of  $G \cdot CO \cdot OR'$ . These coefficients,  $k_H^G$  and  $k_{OH}^G$ , may now be regarded as the polar constituents of those,  $k_H$  and  $k_{OH}$ , of the

series  $R \cdot CO_2R'$ ; they are the values which  $k_H$  and  $k_{OH}$  *would* assume in the presence of a *constant* steric effect arbitrarily fixed by the choice of the form of  $G$ . For the  $n$ th ester considered, let  $k_H = k_H^0/S$ , where  $S$  is a factor introduced to express the effect of steric inhibition in the hydrolytic reaction involving hydrogen ions;  $S$  will clearly depend on  $n$ , that is, on the nature of  $R$ . The value of  $k_{OH}$  will not, of course, be  $k_{OH}^0/S$  because the mechanism of the reaction with hydroxyl ions is different; a different connecting factor will, in general, be required, and may be expressed by  $CS$  in the relation  $k_{OH} = k_{OH}^0/CS$ . Now the basic assumption here made is that, because the difference between hydrogen- and hydroxyl-ion catalysis repeats itself throughout the series of esters of which the hydrolysis is being considered,  $C$  will be independent of  $n$  to a first approximation; in other words, that  $S$ , having been defined for *each* ester by reference to hydrion catalysis, takes sufficient account, for another kind of catalysis, of the varying nature of the esters, leaving the constant  $C$  to take charge, as it were, of the (constant) nature of the second catalyst. It is not expected that  $C$  will be *exactly* constant; but the larger  $C$  is—that is, the more diverse the mechanisms with regard to their susceptibility to steric effects—the more nearly true should be the suggested relation. The constancy of  $C$  being assumed, it follows that  $C(k_{OH}/k_H) = k_{OH}/k_H^0$ , that is, that  $k_{OH}^0/k_H^0$  is a function of polarity only. Similarly, if  $R$  is kept constant and  $R'$  is made to vary,  $C'(k_{OH}/k_H) = k_{OH}^0/k_H^0$ . Finally, both  $C$  and  $C'$  are *arbitrary* constants, since they depend on the forms chosen for  $G$  and  $G'$ ; therefore, the general relationship for all the isotypic esters,  $R \cdot CO_2R'$ , with variable  $R$  and  $R'$ , is that  $k_{OH}/k_H$  is directly proportional to its polar constituent.†

This view, namely, that  $k_{OH}/k_H$  is, probably within wide limits, a function of polarity only, and is untrammelled by the complications due to steric hindrance which affect  $k_{OH}$  and  $k_H$  separately, may be tested by reference to experimental data; and it is convenient to use two types of data for this purpose.

The first uses the theory of the  $v$ - $p_H$  isotherm. That the velocity of an aqueous reaction catalysed by hydrogen and hydroxyl ions must pass through a minimum (at  $p_H = p_H^*$ ) is obvious *a priori*, but was first observed by Wijs for the hydrolysis of methyl acetate

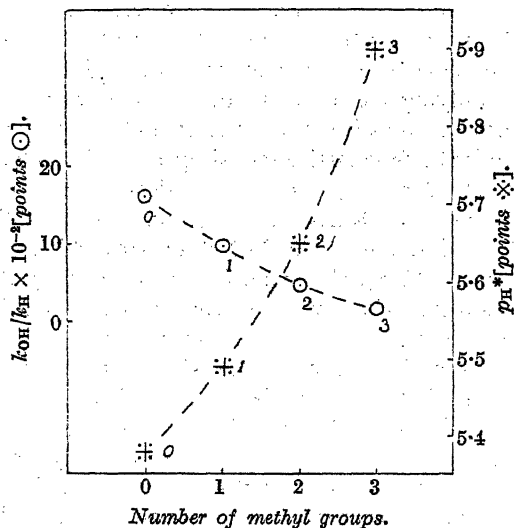
† It will be observed that this conclusion is reached without specific assumptions relating to mechanism. It is necessary only that the mechanisms obtaining should admit the validity of the basic hypothesis, namely, that the relative steric effects on velocity are expressible as the product of two coefficients singly dependent, respectively, on the ester and the catalyst. This granted, it follows that the conclusion drawn should apply to a pair of acid or of basic catalysts, *e.g.*, to  $k_{\text{weak acid}}/k_H$  or to  $k_{\text{weak base}}/k_{OH}$ , as well as to a pair composed of one catalyst of each kind.

(*Z. physikal. Chem.*, 1893, **11**, 492; **12**, 514); and the symmetry of the  $v$ - $p_H$  curve, which is important for the location of the stability maximum, *i.e.*, of  $p_H^*$ , seems to have been first shown by Euler and Hedelius (*Biochem. Z.*, 1920, **107**, 150; compare Euler and Svanberg, *Z. physikal. Chem.*, 1921, **115**, 139, and Euler and Laurin, *Arkiv Kemi, Min. Geol.*, 1920, **7**, No. 30, 1) for the mutarotation of glucose. Dawson, partly with Dean and Hoskins (J., 1926, 2872, 3166; 1927, 213, 1148, 1290), has directed attention to the consequences of applying the (concentration) mass law, amongst which are (a) that the  $v$ - $p_H$  isotherm should be symmetrical because it should be a catenary, (b) that  $-2p_H^* - \log K_w = \log (k_{OH}/k_H)$ , where  $K_w$  is the ionic product of water, and (c) that, when the  $p_H$  variation is produced by a series of buffers of which either the acidic or the saline component is kept constant in concentration, catalysis by the buffer constituents causes some displacement of  $p_H^*$ , but preserves the catenary form of the curve. We are not here concerned with the point (Brönsted and Guggenheim, *loc. cit.*) that relations cannot be absolute which neglect effects due to ionic environment in buffers, because, in applying (b) to calculate  $k_{OH}/k_H$  from observed values of  $p_H^*$ , the fact has to be faced that the available data for  $p_H^*$  neglect the correction for buffer constituents altogether (this defect in method is remedied in Part II). However, despite the approximate character of the data (Karlsson, *Z. anorg. Chem.*, 1921, **119**, 69; 1925, **145**, 1; Bolin, *ibid.*, 1925, **142**, 201; 1928, **177**, 227; compare Dawson, J., 1927, 1148), the examples to which they apply are so diverse that the general character of the suggested relation between  $k_{OH}/k_H$  and polarity can be observed over a greater range of structural variation than it is at present possible to traverse in any other way. From the first series in Table I, it will be seen that  $k_{OH}/k_H$  increases regularly, as it should, with the efficacy of the electron-sink; it is also noteworthy that the polar group may act from either of the residues attached to  $-CO\cdot O-$ . Ester No. 2 was glycerol monoacetate, but is formulated, for convenience in tabulation, as though it were glycol monoacetate, for the polar effect of the terminal  $\cdot CH_2\cdot OH$  group is expected to be negligible. Ester No. 5 was actually ethyl aminoacetate; but the velocity minimum occurs at  $p_H$  3.5, *i.e.*, in *acid* solution, so that the entity to which  $k_{OH}/k_H$  refers is the ammonium kation, and this agrees with the very high value of  $k_{OH}/k_H$ . The value of  $k_{OH}/k_H$  for methyl formate, regarded as the parent of the second series in Table I, is not known; but it is known qualitatively to be considerably greater than for ethyl formate. In this series, the value of  $k_{OH}/k_H$  diminishes, as it should, with the efficacy of the electron-source, which, as before, may act from either of the groups attached to  $-CO\cdot O-$ .

TABLE I.

No.	X.	Y.	$p_H^*$ .	Temp.	$K_w \cdot 10^{14}$ .	$(k_{OH}/k_H) \times 10^{-3}$ .
<i>First Series: X-CH<sub>2</sub>-CO-O-CH<sub>2</sub>-CH<sub>2</sub>-Y.—Effect of electron-sink.</i>						
1	H-	H-	5.36	25°	1.0	2
2	H-	HO←	5.0	25	1.0	10
3	Cl←	H-	4.8	20	0.8	32
4	MeCO←	H-	4.4	25	1.0	160
5	⊕NH <sub>3</sub> ←	H-	3.5	20	0.8	12,000
<i>Second Series: X-CO-O-CH<sub>2</sub>-Y.—Effect of electron-source.</i>						
1	H-	H-	—	—	—	Large
2	H-	CH <sub>3</sub> →	4.65	20	0.8	63
3	CH <sub>3</sub> →	H-	5.15	25	1.0	5
4	CH <sub>3</sub> →	CH <sub>3</sub> →	5.36	25	1.0	1.9
5	CH <sub>3</sub> →	CH <sub>3</sub> →CH <sub>2</sub> →CH <sub>2</sub> →	5.65	25	1.0	0.5

In the above examples there is a certain variety in the types of polar substituents, and, accordingly, a very great diversity in the



Rates of hydrolysis of methylacetic esters as function of structure.

values of  $k_{OH}/k_H$ ; and one of the advantages of this method of estimating  $k_{OH}/k_H$  is that the ease with which the ratio is determined is independent of its order of magnitude, at least between  $10^2$  and  $10^7$ . When the order of magnitude of the ratio becomes greater than  $10^8$ , difficulties enter the independent *direct* determination of  $k_{OH}$  and  $k_H$  at the same temperature,† and, therefore, the range

† The numerous alleged determinations of  $k_{OH}$  in buffers, but without correction, or data permitting the application of a correction, for the buffer constituents, are, of course, valueless, except as indications of order of magnitude.

of polar substituents which can be examined by reference to data of this kind is more restricted; on the other hand, the values of  $k_{OH}/k_H$  thus obtained should be more accurate than those derived from stability maxima in the absence of a correction for the buffer, and should therefore suffice to distinguish the effects of finer polar differences. In illustration, reference may again be made to the apparently anomalous series of simple alkyl acetates tabulated at the outset. The calculated values of  $k_{OH}/k_H$  are as shown in Table II, and it will be seen that in these values there is no perceptible anomaly; if plotted against the number of  $\beta$ -methyl groups,  $k_{OH}/k_H$  and  $p_H^*$  both give smooth uninflected curves of small curvature (see fig.).

TABLE II.

Acetate (25°). $(k_{OH}/k_H) \times 10^{-2}$ .	$p_H^*$ .	Source of $k_{OH}$ and $k_H$ .
$CH_3$	16.1	5.39 Means from literature.
$CH_3 \rightarrow CH_3$	9.9	5.50 "
$(CH_3)_2 \rightarrow CH$	4.7	5.66 Means from "b, c ( $k_{OH}$ ) and a, c ( $k_H$ ).
$(CH_3)_3 \rightarrow C$	1.5	5.91 Means from b, c ( $k_{OH}$ ) and c, d ( $k_H$ ).

References: (a) Palomaa, *loc. cit.*; (b) Olsson, *Z. physikal. Chem.*, 1925, **118**, 107; (c) Skrabal and Hügetz, *loc. cit.*; (d) Olsson, *Z. physikal. Chem.*, 1927, **125**, 243; 1928, **133**, 233.

Having explained the *a priori* considerations on which this series of investigations will be based, and illustrated their reasonableness by reference to existing data, the object of this introductory communication is accomplished. Any estimate of the extent to which the method outlined can be pressed in the analytical separation of the two main constitutional influences which affect the stability of esters towards hydrolysis must await a wider range of data such as will be provided in ensuing papers.

THE UNIVERSITY, LEEDS.

[Received, March 5th, 1930.]

### CXXX.—*The Mechanism of, and Constitutional Factors controlling, the Hydrolysis of Carboxylic Esters. Part II. Hydrolytic Stability Maxima of some Glyceric Esters.*

By CONSTANCE MARY GROOCCOCK, CHRISTOPHER KELK INGOLD,  
and ARTHUR JACKSON.

IN selecting a method for the determination of catalytic data of the type of which the significance is discussed in Part I, our object was to combine wide applicability with some approach to accuracy,

The first consideration suggested the location of hydrolytic stability maxima, since, as has already been shown, this is the only method which remains practicable when strongly electron-attracting substituents adjoin the ester residue.

The second desideratum required that such a process be used only in conjunction with an adequate method for eliminating catalytic influences associated with the buffers used to define the  $p_H$ . These influences consist of (a) the superimposed catalysis of the buffer acid and buffer base, and (b) the effect of the buffer-ion environment on the activity of all the catalytic entities. A method for their elimination has been devised and is described later.

A third preliminary consideration was necessitated by the sparing solubility of the majority of esters,  $R \cdot CO_2R'$ , in water. The objections to the use of a mixed solvent, such as aqueous alcohol, for our purpose are obvious and are of a type not easy to surmount; it was therefore decided to avoid the difficulty by varying the radicals  $R$  and  $R'$  separately and using a poly-hydroxylated group for the radical which is kept constant throughout any given series. In this paper, for example, we record the results obtained with a series of glyceric esters  $CH_2(OH) \cdot CH(OH) \cdot CO \cdot OR$  ( $R$  variable).

Previous investigators who have undertaken experiments with the object of locating the hydrolytic stability maxima of esters in buffer solutions appear always to have aimed at using a sufficient buffer concentration to stabilise the  $p_H$  against disturbance from the acid liberated from the hydrolyte in the course of the experiment. This method involves two difficulties. First, the necessary concentration of buffer materials (which have to be neutralised in the course of the analytical work) is often such that the titre which measures the progress of hydrolysis is of the order of 1% of the total titre; and this sets a rather low limit to the accuracy obtainable in analysis. Secondly, in the present state of electrolytic theory there is no method for extrapolating to zero buffer concentration the velocity data obtained with concentrated buffer solutions, which is sufficiently trustworthy to obviate the necessity for an empirical check by reference to experimental data for low buffer concentrations; and this necessary empirical control is clearly impossible in a method in which, at the lowest buffer concentrations which are consistent with its principles, the buffer substances are still by far the main constituents of the solution. The first of these objections could, of course, be minimised by the use of gravi-volumetric methods of analysis; but since there seemed no way of overcoming the second, we rejected the method in favour of the following process.

An aqueous solution of the glyceric ester (concentration  $E_0$ ) was treated with sufficient carbonate-free sodium hydroxide to hydrolyse



a small proportion of it. At the temperature used, saponification occurred almost instantly with formation of sodium glycerate (concentration  $c$ ), and in a few moments the solution passed through the neutral point and became faintly acid. It is easily seen that, from the moment of neutrality onwards, all effects on the dynamics of the reaction will be substantially the same as if sodium glycerate had been added at that moment to an ester solution of concentration  $E = E_0 - c$ . This sodium glycerate constituted the (constant) salt constituent of the buffer series,  $c\text{NaA} + x\text{HA}$ . The glyceric acid liberated in concentration  $x$  during the continuation of hydrolysis furnished the (variable) acid constituent of the buffer series, and also the measure of the decomposition of the hydrolyte.

In considering the dynamics of a hydrolysis subject to this kind of  $p_H$  control, it is convenient to treat effects (a) and (b) (see p. 1040) separately. First, we shall disregard effects due to buffer-ion environment. In symbolising the dynamics we shall follow the procedure developed by Dawson.

Application to the fundamental equation

$$v = v_H + v_{OH} + v_m + v_a + v_w = k_H[H^+] + k_{OH}[OH'] + k_m[HA] + k_a[A'] + k_w[H_2O]$$

of the mass-law relations

$$[A'] = c + [H^+] \text{ and } [HA] = c[H^+]/K + [H^+]^2/K \quad (1)$$

leads to

$$v = \left(k_H + \frac{k_m c}{K} + k_a\right)[H^+] + \frac{k_{OH} K_w}{[H^+]} + \frac{k_m}{K} [H^+]^2 + (k_a c + k_w [H_2O]) \quad (2)$$

of which

$$v = \left(k_H + \frac{k_m c}{K}\right)[H^+] + \frac{k_{OH} K_w}{[H^+]} + (k_a c + k_w [H_2O]) \quad (3)$$

is an approximate form. The approximation consists in the neglect of  $[H^+]$  in comparison with  $c$ , and so long as the former is of the order  $10^{-4.5}$  and the latter of order  $10^{-1}$  this is justifiable. The quantities,  $v = u$  and  $[H^+] = h$ , characterising the relation  $dv/d[H^+] = 0$  are given by

$$u = 2 \left\{ k_{OH} K_w \left( k_H + \frac{k_m c}{K} \right) \right\}^{\frac{1}{2}} + (k_a c + k_w [H_2O]) \quad (4)$$

and

$$h = \left\{ k_{OH} K_w \left( k_H + \frac{k_m c}{K} \right) \right\}^{\frac{1}{2}} \quad (5)$$

and, if  $w$  is written for that part of  $v$  which is independent of  $[H^+]$ , the approximate equation (3) for  $v$  takes a form equivalent to that

used by Dawson to express the symmetry of the  $v$ - $p_H$  relation, viz.,

$$2 \frac{v-w}{u-w} = \frac{[H^*]}{h} + \frac{h}{[H^*]} \quad (6)$$

In using this form for the purpose of deriving an equation for the experimentally determined  $x$ - $t$  relation, we should substitute for  $v$  and  $[H^*]$ , using

$$dx/dt = v(E-x) \quad (7)$$

and

$$K(x - [H^*]) = [H^*](c + [H^*]) \quad (8)$$

but if the second of these equations is replaced by  $[H^*] = Kx/c$ , the approximation (except at the commencement of the reaction) is of the same order as that introduced above, and the differential equation takes the comparatively simple form

$$\frac{dx}{dt} = (E-x) \left\{ \frac{1}{2}(u-w) \left( \frac{Kx}{hc} + \frac{hc}{Kx} \right) + w \right\} \quad (9)$$

The manner in which the solution of equation (9) should be expressed in order that it may be real depends on the relative magnitudes of  $u$  and  $2w$ . In our experiments  $u$  was always greater than  $2w$ , and the real form of the solution for this case is

$$t \left\{ \frac{E^2 K^2}{h^2 c^2} + \frac{2EKw}{(u-w)hc} + 1 \right\} = EK \log_e \left[ \frac{E}{E-x} \left\{ \frac{K^2 x^2}{h^2 c^2} + \frac{2Kwx}{(u-w)hc} + 1 \right\} \right] \\ - \frac{(u-w)hc - EKw}{\sqrt{u^2 - 2uw}} \left\{ \tan^{-1} \frac{\frac{(u-w)Kx}{hc} + w}{\sqrt{u^2 - 2uw}} - \sin^{-1} \frac{w}{u-w} \right\} \quad (10)$$

From numerical data conforming to this equation it is obviously possible to construct the curve of equation (3) or its equivalent (6), and also the  $(dx/dt)$ - $x$  curve (equation 9).

It is now necessary to consider the effect of varying  $c$ . Since, for a given value of  $[H^*]$ , equation (2) may be written

$$v = A + \left( \frac{k_m [H^*]}{K} + k_a \right) c \quad (11)$$

it follows that, in so far as the mass law expresses the situation,  $v$  is a linear function of  $c$  for constant  $[H^*]$ , and  $dv/dc$  is a linear function of  $[H^*]$ . If, therefore, we use a family of experimentally obtained  $x$ - $t$  curves to plot a corresponding family of  $v$ - $[H^*]$  curves, and then employ them to construct a family of  $v$ - $c$  curves, the last should be straight lines. Their intercepts on the axis  $c = 0$  should yield the data required for the construction of a  $v$ - $[H^*]$  curve corresponding with  $c = 0$ , and their slopes should give a  $(dv/dc)$ - $[H^*]$  curve, of

which the slope measures  $k_m/K$  and the intercept on the axis  $[H^+] = 0$  measures  $k_a$ . The mass-law expression for the  $(v-[H^+])_{c=0}$  curve is

$$v_0 = (k_H + k_a)[H^+] + \frac{k_{OH}K_w}{[H^+]} + \frac{k_m}{K}[H^+]^2 + k_w[H_2O]. \quad (12)$$

but the practical simplification which results from applying the above procedure to our experimental data is greater still, because, although only rough estimates of  $k_a$  and  $k_m$  are possible, it transpires that  $k_a/k_H$  is of the order  $10^{-4}$ , and that in the neighbourhood of the stability maximum  $k_m[H^+]/K$  is of the same order as  $k_a$ ; that is, there are reasons, justifying the omission of the terms  $k_a[H^+]$  and  $k_m[H^+]^2/K$  from equations (2) and (12), which are independent of the reason that applies in the case of equation (2) when  $c$  is great in comparison with  $[H^+]$ ; the last reason therefore still holds good when  $c = 0$ , and the equation for the  $v_0-[H^+]$  curve may be expressed

$$v_0 = k_H[H^+] + \frac{k_{OH}K_w}{[H^+]} + k_w[H_2O] \quad (13)$$

If  $w_0$  is written for  $k_w[H_2O]$ , the corresponding data for the stability maximum in the absence of buffer substances are

$$u_0 = 2\sqrt{k_H k_{OH} K_w} + w_0 \quad (14)$$

$$h_0 = \sqrt{k_{OH} K_w / k_H} \quad (15)$$

and, in terms of these quantities, the equation for  $v_0$  is

$$2 \frac{v_0 - w_0}{u_0 - w_0} = \frac{[H^+]}{h_0} + \frac{h_0}{[H^+]} \quad (16)$$

The above outline of the method we have adopted in order to eliminate from our results effects due to the catalytic activity of the constituents of the buffers, leaves untouched the question of correcting for disturbances due to the effect of ion-environment on catalytic activity. Brönsted, in particular, has drawn attention to the importance of these influences in homogeneous catalysis. Now, Dawson and his collaborators have also envisaged this problem, and, although we must agree with Brönsted that recognition of the disturbances mentioned is equivalent to an admission that mass-law relations are inapplicable, what is of more importance is that Dawson has found a simple method of giving a quantitative account of the actual catalytic relations; and his method may be expressed in the statement that the *form* of the mass-law equations holds good provided that the coefficients are no longer regarded as constants, but are replaced by suitable *functions of the ionic strength*. Dawson and Key, for instance, investigated the effect of neutral salts on the catalysis of the iodination of acetone (J., 1928, 1248), and found

that, with one exception, the deviations from constancy which it was necessary to ascribe to the catalytic coefficients were barely detectable. For the one coefficient (namely,  $k_H$ ) for which the variation could be measured, it was found to be represented by a linear function of the ionic strength over a very much greater range of ionic strength than any with which we are concerned. It can readily be shown (i) that, if conditions which are similar in regard to the orders of magnitude of the quantities involved hold also for ester hydrolysis, then the main effect on the relations which equation (11) purports to express will be represented by an alteration in the slope of the  $v$ - $c$  curves (because, of course,  $A$  contains  $k_H$ ); and (ii) that the variations attributable to  $k_m$  and  $k_a$  are unlikely in practice to impart any perceptible curvature to these graphs within the range of concentration used in our experiments. Again, Dawson and Lowson have made a study of salt effects on the hydrolysis of ethyl acetate in which they have considered especially the deviations with increasing salt concentration which must be ascribed to the dissociation constants of weak acids (J., 1929, 1217). They found that the variability with which it is necessary to credit these constants is of the type required by the Debye-Hückel theory of electrolytes, although there remained a divergence from that theory in the matter of the numerical value of one of the constants of the equation connecting  $K$  with  $c$ . The effect of influences of this nature on the relations which equation (11) is supposed to represent can be qualitatively deduced, although they are somewhat complicated. There will be, for instance, an effect on the explicit  $K$ ; this is calculated to impart to the  $v$ - $c$  curves a convexity towards the  $c$ -axis, which might be large enough to be perceptible on the acid side of the stability maximum, but would be extremely slight on the alkaline side. On the other hand, there will be an indirect effect on  $v$  arising from the fact that  $v$  is a function of  $[H^+]$ , which is a function of  $K$ ; and this should produce a slight convexity towards the  $c$ -axis on the acid side of the stability maximum. Similarly, opposing effects, relating primarily to the alkaline side of the stability maximum, can be foreseen; and the general conclusion which emerges from a consideration of the probable orders of magnitude of the quantities involved is that the main effect of the disturbances considered would again be represented by an alteration of the slope of the  $v$ - $c$  curves, although small departures from linearity remain theoretically possible. Further details with regard to the theoretical aspect of this matter need not be discussed, because we find that, for the range of salt concentration employed, the  $v$ - $c$  curves are, in fact, straight lines to within the limits of consistency of the data. It is, therefore, clear that the process of linear extrapolation outlined above must

yield velocity values ( $v_0$ ) which are not only independent of contributory catalysis by the buffer constituents, but are also free from the disturbing effects of buffer-ion environment on catalytic activity; in other words, the  $v_0$ -[H<sup>+</sup>] curve obtained from the experimental data by the method indicated should be represented, to a degree of accuracy determined only by the data themselves, by equations (13—16), in which all the quantities pertain to salt-free aqueous solutions.

There is one disturbing factor which cannot be eliminated by any such method as that outlined, and that is the effect of the ester itself in modifying the properties of the aqueous medium. Knowing nothing about this, we have been forced to neglect it; but inasmuch as it is proposed later to compare the results obtained, we have endeavoured to arrange that effects due to the ester shall be kept as nearly constant as possible throughout the series by using, in every case, solutions of uniform ester concentration.

Eight esters of *dl*-glyceric acid with alcohols of simple constitution have been examined by the method described. The results are summarised in Section E of the experimental part of this paper (see especially Table IX and Figs. 4 and 5). Discussion of the data is postponed until the results of further experiments, now in progress, are available for collective consideration.

#### EXPERIMENTAL.

(A) *Materials*.—*dl*-Glyceric acid was prepared by oxidation of glycerol with nitric acid ("Beilstein," 4th Aufl., III, 395). Its esters with aliphatic alcohols have hitherto usually been obtained by heating the acid with the alcohol at 180—190° (Frankland and McGregor, J., 1893, 63, 512; Frankland and Price, J., 1897, 71, 253), but we found that esters prepared by this method turned brown on keeping. The esters were therefore prepared by boiling the acid (it is not necessary that it should be absolutely anhydrous) with an excess of the alcohol containing 1% of hydrogen chloride. Careful fractionation under diminished pressure yielded stable, colourless esters of constant b. p., which, however, contained traces of chlorine compounds. These were removed by distillation under reduced pressure with freshly prepared silver oxide. The esters appeared to be somewhat hygroscopic, and, accordingly, precautions were taken to prevent access of moisture. Purity was checked by quantitative saponification ( $G$  = glyceryl group). The italics in Table I indicate the esters which are new.

(B) *Calibration*.—In order to obtain a convenient rate of reaction in the neighbourhood of the stability maxima it was found necessary to use a temperature considerably above that of the room. Since

TABLE I.

<i>dl</i> -Glycerate.	B. p.	G (found), %.	G (calc.), %.
Methyl .....	123—125°/10 mm.	74.16, 74.00	74.20
Ethyl .....	126.5°/10 mm.	66.50, 66.60	66.40
<i>n</i> -Propyl .....	128—129°/10 mm.	60.13	59.94
<i>iso</i> Propyl .....	126—127°/11 mm.	59.87	59.94
<i>n</i> -Butyl .....	127—129°/10 mm.	54.72	54.91
<i>iso</i> Butyl .....	117°/9 mm.	54.86	54.91
<i>n</i> -Amyl .....	134—136°/11 mm.	50.43	50.56
<i>iso</i> Amyl .....	135—137°/11 mm.	50.45	50.56

the titrations were carried out at room temperature, the ordinary methods for the intercalibration of volumetric apparatus were inapplicable on account of thermal expansion. We therefore standardised the barium hydroxide solution used for the acidimetric measurements by a method which included an automatic relative calibration of the series of flasks and pipettes used against the already internally calibrated burette. The procedure may be illustrated as follows.

Pure succinic acid (1.2832 g.) was placed with distilled water in a flask, A, which had a mark on the neck, and the solution was made up with water to the mark at 70.2°. At this temperature a sample was withdrawn with a nominally 25 c.c. pipette, (a), and titrated, in the presence of an approximately standard quantity of phenolphthalein, with nominally *N*/40-barium hydroxide, 39.38 ml. of which were required to produce the tint which throughout these experiments was accepted as an indication of the end-point. The capacity of the flask, up to its mark, at the same temperature, was determined gravimetrically, allowance being made for the buoyancy of water in air, and found to be 539.2 ml. It follows that each ml. of titre corresponds with the presence of 0.0010265 g.-equiv. of acid per litre in a solution the sample of which has been withdrawn at the temperature stated from flask A by pipette (a). This temperature was used throughout the velocity measurements. Flasks B—F were treated similarly in relation to pipette (a); later, another set G—K were treated likewise in relation to a second pipette (b).

(C) *Details of a Typical Experiment* (Expt. L, 1.15).—A mixture of methyl glycerate (see Table I) (42.004 g.), warm distilled water (about 400 c.c.), and 0.9746*N*-sodium hydroxide (83.01 ml.) in flask A was placed in the thermostat, and, after temperature equilibrium had been attained, the whole was made up to the mark. At intervals extending over about a week, samples were withdrawn with pipette (a) and titrated in the manner described in Section B. The results are given in the 2nd, 3rd, and 4th columns of Table II, *t* being the time (in minutes) and *x* the normality of the acidity.

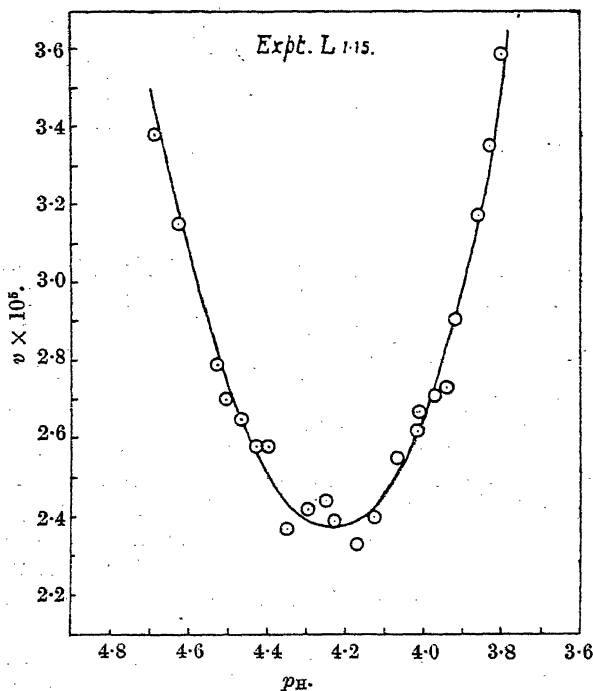
TABLE II.

Observation No.	$t$ .	Titre, ml.	$x$ .	$t$ (calc.).	Deviation in $t$ .
1	271	10.74	0.01102	(271)	
2	390	12.75	0.01309	392	- 2
3	562	15.41	0.01581	563	- 1
4	714	17.55	0.01802	714	$\pm$ 0
5	1075	22.10	0.02268	1068	+ 7
6	1395	25.92	0.02660	1398	- 3
7	1668	29.13	0.02990	1676	- 8
8	1887	31.25	0.03208	1877	+10
9	2165	34.54	0.03545	2167	- 2
10	2806	41.32	0.04241	2812	- 6
11	3228	45.67	0.04688	3226	+ 2
12	3651	50.11	0.05144	3650	+ 1
13	4345	57.77	0.05930	4348	- 3
14	4802	62.86	0.06452	4798	+ 4
15	4998	65.16	0.06688	4999	- 1
16	5744	73.60	0.07556	5734	+10
17	6222	79.29	0.08141	6217	+ 5
18	7105	90.38	0.09277	7105	$\pm$ 0
19	7615	96.94	0.09951	7620	- 5
20	8359	107.19	0.11003	8374	-15

From the data given it can be calculated that  $E = 0.4988$  and  $c = 0.1500$ . The times recorded in the 5th column of Table II are calculated from an equation equivalent to (10), the values used being  $K = 2.28 \times 10^{-4}$ ,  $u = 2.37 \times 10^{-5}$ ,  $w = 0.37 \times 10^{-5}$ , and  $h = 8.81 \times 10^{-5}$ . The value of  $K$  is taken from Ostwald's measurements at  $25^\circ$  (*Z. physikal. Chem.*, 1889, 3, 192), and its selection is admittedly arbitrary, because, apart from other considerations (see below), the temperature is not that of our experiments. No determinations of  $K$  appear to have been made at higher temperatures, and we have not attempted to introduce a temperature correction by means of special experiments, for the following reasons. First, judging from such evidence as is available, the thermal variations in the dissociation constants of simple monocarboxylic acids are so slight that they are difficult to estimate with accuracy, either from conductivities, or from heats of neutralisation, except on the basis of an elaborate investigation. Secondly, the correction, if it could be estimated, would probably be smaller than the uncertainty in the value for the basic temperature,  $25^\circ$ ; Böeseken, for instance, records  $2.8 \times 10^{-4}$  for this temperature (*Rec. trav. chim.*, 1918, 37, 169). Thirdly, as is pointed out in the introduction, our experiments are necessarily affected by the circumstance that our buffer-free solvent is, not water, but an aqueous solution of the ester; whilst this disturbing influence inevitably affects  $K$  (and there is no point in attempting to eliminate it, since the same cannot be done for the other coefficients and constants involved), it would be superfluous to endeavour to eliminate from  $K$  the (probably smaller) disturbance

due to temperature. In the circumstances, the best course seemed to be to adopt a definite value of  $K$  and keep to it throughout the work; and since the effects mentioned would probably tend to reduce  $K$ , we have chosen the lower of the two recorded values. Errors due to an incorrect value of  $K$  should, we think, be constant throughout the series of experiments, because, as has been explained, all effects (including the one on  $K$ ) due to the main *variable* factor, namely, the salt concentration, are eliminated during the reduction of our

FIG. 1.



results to those which should pertain to the buffer-free medium. The  $x-t$  curve plotted from the figures in Table II runs generally upwards and to the right, but contains a point of inflexion (minimal slope) in the neighbourhood of the 10th observation. Of the three values  $u$ ,  $w$ , and  $h$  selected to give that degree of agreement with equation (10) which is indicated in the 6th column,  $u$  is mainly responsible for the general slope,  $w$  controls the degree of acuteness of the inflexion, and  $h$  its position. It should be added that, since there is a certain indefiniteness about the time of starting, and also because the integrated formula is not accurate near the commencement of the reaction, the first observation was treated as the effective



starting point for computation; \* this is indicated by the parenthesis at the top of the table.

The general nature of the  $x-t$  relation can be more clearly exhibited by using the differences between neighbouring observations to calculate  $v$  from equation (7) and the means of such observations to obtain corresponding values of  $[H^+]$  (or  $p_H$ ) from equation (8). The results of this calculation are given in Table III, the figures in the last two columns of which are graphically represented in Fig. 1.

In the table, col. 1 enables the pair of observations used to be identified in Table II; cols. 2 and 3 record respectively the differences of time and of acidity; col. 4 gives the mean acidity for each interval; and cols. 5 and 6 record the mean molecular concentrations of glyceric acid and of glyceric ester for each interval. It will be seen that only about one-fifth of the total possible reaction has been followed (in the majority of our experiments the fraction is smaller), and for this reason, having regard to Dawson and Lowson's investigation of the effect of reversibility on the dynamics of the hydrolysis of ethyl acetate (J., 1927, 2107), we need not fear serious disturbance from the retrograde reaction.

TABLE III.

Nos.	$\Delta t$ .	$\Delta x$ .	$x$ (mean).	$x - [H^+]$ .	$E - x$ .	$v \times 10^5$ .	$p_H$ .
1-3	291	0.00479	0.0134	0.0134	0.4854	3.38	4.69
2-4	324	0.00493	0.0155	0.0155	0.4833	3.15	4.63
3-5	513	0.00687	0.0192	0.0192	0.4796	2.79	4.53
4-5	362	0.00466	0.0203	0.0203	0.4785	2.70	4.51
4-6	681	0.00858	0.0223	0.0223	0.4765	2.65	4.47
5-6	320	0.00392	0.0247	0.0247	0.4741	2.58	4.43
5-7	593	0.00722	0.0263	0.0263	0.4725	2.58	4.40
6-8	492	0.00548	0.0293	0.0293	0.4695	2.37	4.35
7-9	497	0.00555	0.0327	0.0326	0.4661	2.42	4.30
8-10	919	0.01033	0.0372	0.0371	0.4616	2.44	4.25
9-10	641	0.00706	0.0390	0.0389	0.4598	2.39	4.23
10-11	422	0.00447	0.0446	0.0445	0.4542	2.33	4.17
11-12	420	0.00456	0.0492	0.0491	0.4496	2.40	4.13
12-13	694	0.00786	0.0554	0.0553	0.4434	2.55	4.07
13-14	457	0.00522	0.0619	0.0618	0.4369	2.62	4.02
13-15	653	0.00758	0.0631	0.0630	0.4357	2.67	4.01
14-16	942	0.01104	0.0700	0.0699	0.4288	2.71	3.97
15-16	746	0.00868	0.0712	0.0711	0.4276	2.73	3.96
16-17	478	0.00585	0.0785	0.0783	0.4203	2.90	3.92
17-18	883	0.01136	0.0921	0.0919	0.4067	3.17	3.86
18-19	500	0.00674	0.0961	0.0959	0.4027	3.35	3.83
19-20	744	0.01052	0.1047	0.1045	0.3941	3.58	3.80

It will be obvious from Fig. 1 that the experimental data correspond with a curve approximating more or less closely to the usual

\* To do this we replace  $t$  (equation 10) by  $t - t_1$ , remove the term  $\sin^{-1}$  (an integration constant), and subtract from the right-hand side of the residual equation an expression identical with that side except that  $x_1$  replaces  $x$ , ( $x_1$ ,  $t_1$ ) being the first observation.

catenary form; the main purpose of the figure, however, is to exhibit the fact that the accuracy of the individual observations is insufficient to enable directly read differences to define the  $v$ - $p_H$  curve with any approach to precision (the curve drawn is constructed as described below). Our practice in this and the other experiments has therefore been to plot the  $x$ - $t$  observations, and to read  $dx/dt$  from the curve. We regard this method of eliminating the casual errors of individual observations as allowable because it is a close graphical analogue to many accepted legitimate methods of attaining the same end, as, for instance, the averaging of a column of individually calculated velocity coefficients derived by the application of an integrated formula to a series of observations tracing the progress of a reaction; indeed, the latter process is, if anything, more difficult to defend because integration itself involves an averaging of errors which might seriously affect direct application of the data to the differential equation to which they should correspond. In applying the graphical process indicated, we found it convenient to plot  $1000x \cos \theta - 0.01t \sin \theta$  against  $100x \sin \theta + 0.001t \cos \theta$ , where  $\theta$  is an angle shown to be suitable by a preliminary rough plot of  $x$  against  $t$ . This method avoids the use of an inconveniently extended scale; the effect is much as if the  $x$ - $t$  data were plotted on a sheet of rubber which was then stretched 10-fold in a direction at right-angles to the general direction of the curve in order to bring into relief the deviations of the points from the curve. For the experiment now considered  $45^\circ$  is a suitable value for  $\theta$ . Proceeding in this way, we obtained the data shown in Table IV, the headings of the first five columns of which are self-explanatory. The velocity values in col. 6 are calculated from equation (6) by use of the values of  $u$ ,  $w$ , and  $h$  given above. Col. 7 shows the deviations, which are seen to be small and casual in character.

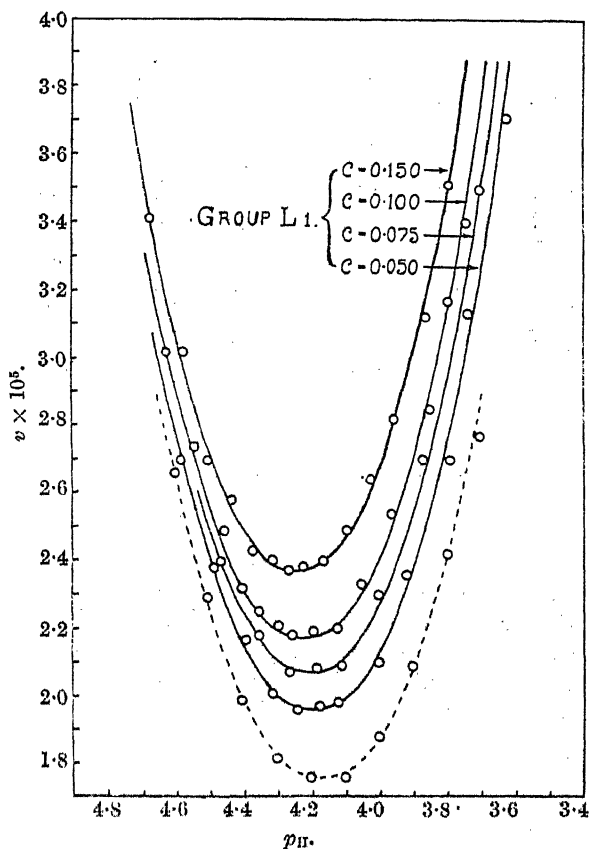
TABLE IV.

 $v \times 10^5$ .

$x$ .	$10^5 \cdot dx/dt$ .	$p_H$ .	$E - x$ .	Found.	Calc.	Diff.
0.0141	1.653	4.67	0.4847	3.41	3.41	$\pm 0.00$
0.0177	1.453	4.57	0.4811	3.02	2.98	$+0.04$
0.0208	1.290	4.50	0.4780	2.70	2.73	$-0.03$
0.0246	1.224	4.43	0.4742	2.58	2.56	$+0.02$
0.0281	1.144	4.37	0.4707	2.43	2.46	$-0.03$
0.0315	1.121	4.31	0.4673	2.40	2.39	$+0.01$
0.0382	1.045	4.26	0.4606	2.37	2.37	$\pm 0.00$
0.0400	1.046	4.22	0.4588	2.38	2.37	$+0.01$
0.0454	1.088	4.16	0.4534	2.40	2.40	$\pm 0.00$
0.0541	1.108	4.09	0.4447	2.49	2.48	$+0.01$
0.0621	1.153	4.02	0.4367	2.64	2.62	$+0.02$
0.0725	1.201	3.95	0.4263	2.82	2.82	$\pm 0.00$
0.0924	1.268	3.86	0.4064	3.12	3.17	$-0.05$
0.1065	1.377	3.79	0.3923	3.51	3.52	$-0.01$

The data in the third and fifth columns enable the  $v$ - $p_H$  curve to be located to within  $\pm 0.01$  unit of  $p_H$  and of  $v \times 10^5$ , except at a distance from the stability maximum where the uncertainty of  $v$  is somewhat greater. The curve is practically symmetrical about the ordinate  $p_H = 4.24$ .

FIG. 2.



(D) *Summary of a Typical Group of Experiments (Group L1).*—This group consists of four experiments of the same nature as that particularised in Section C. 0.5*M*-Methyl glycerate (*E*) was employed throughout, but the concentration of sodium glycerate (*c*) was different in each experiment, being 0.050 in the first, 0.075 in the second, 0.100 in the third, and 0.150 in the fourth. The second experiment was carried out about a year before the other three, which were done contemporaneously; this is mentioned in order to show that during the rather long period over which the measurements

recorded in this paper have extended, a satisfactory constancy of conditions has been maintained.

Proceeding as described in the previous section, we obtained the values of  $v$  and  $p_H$  shown in Table V. The plot of these results is exhibited in Fig. 2 (full-line curves).

TABLE V.

$c = 0.050.$		$c = 0.075.$		$c = 0.100.$		$c = 0.150.$	
$p_H.$	$10^5 v.$	$p_H.$	$10^5 v.$	$p_H.$	$10^5 v.$	$p_H.$	$10^5 v.$
—	—	—	—	4.62	3.02	4.67	3.41
4.85	2.70	—	—	4.54	2.74	4.57	3.02
4.48	2.38	—	—	4.45	2.49	4.50	2.70
4.39	2.17	4.46	2.40	4.40	2.32	4.43	2.58
4.31	2.01	4.35	2.18	4.35	2.25	4.37	2.43
4.24	1.96	4.26	2.07	4.29	2.21	4.31	2.40
4.17	1.97	4.18	2.08	4.25	2.18	4.26	3.37
4.12	1.98	4.11	2.09	4.19	2.19	4.22	3.38
4.00	2.10	4.00	2.30	4.12	2.20	4.16	2.40
3.92	2.36	3.87	2.70	4.05	2.33	4.09	2.49
3.79	2.70	3.70	3.50	3.96	2.54	4.02	2.64
3.73	3.13	—	—	3.85	2.85	3.95	2.82
3.63	3.71	—	—	3.79	3.17	3.86	3.12
—	—	—	—	3.74	3.40	3.79	3.51

It will be seen from the figure that as  $c$  increases, the minimal velocity increases and becomes displaced towards regions of lower hydron concentration, as might have been expected on the basis of equations (4) and (5).

From these curves the  $v$ - $c$  curves can readily be plotted. They are shown in Fig. 3 for each 0.1 unit of  $p_H$  from  $p_H$  4.6 to  $p_H$  3.8 inclusive, the numerals showing the  $p_H$  value to which each point corresponds. When points relating to the same  $p_H$  are joined, straight lines are obtained which, on production to the axis of velocities, yield the velocity data which should pertain to the salt-free solution.

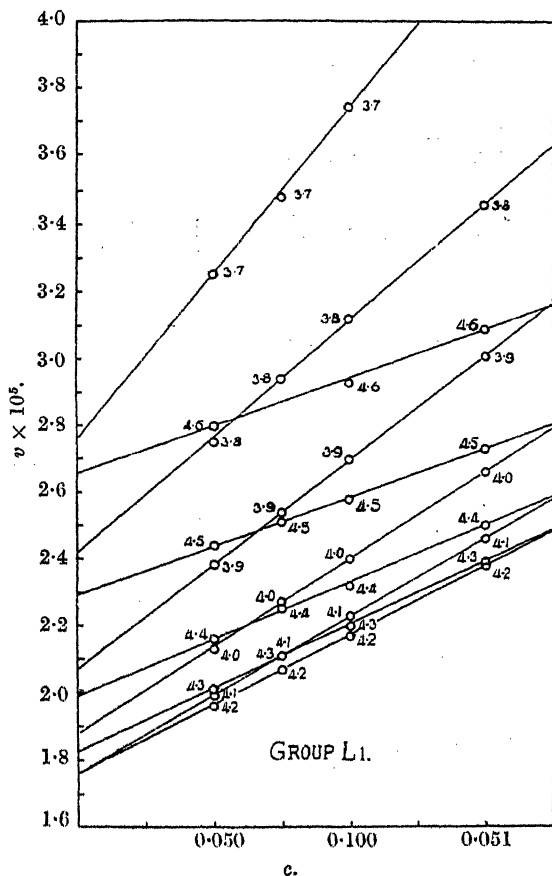
The data obtained from the intercepts on the axis of velocities are shown in connexion with the lowest (broken) curve of Fig. 2. They are compared in Table VI with the requirements of equation (16), in which the values used are  $h_0 = 6.76 \times 10^{-5}$ ,  $u_0 = 1.76 \times 10^{-5}$ , and  $w_0 = 0.06 \times 10^{-5}$ .

TABLE VI.

$p_H$ .....	4.6	4.5	4.4	4.3	4.2
$10^5 v_0$ .....	2.66	2.29	1.99	1.82	1.76
$10^5 v_0$ (calc.) .....	2.67	2.27	1.99	1.83	1.76
Diff. ....	-0.01	+0.02	$\pm 0.00$	-0.01	$\pm 0.00$
$p_H$ .....	4.1	4.0	3.9	3.8	
$10^5 v_0$ .....	1.76	1.89	2.09	2.42	
$10^5 v_0$ (calc.) .....	1.78	1.89	2.08	2.43	
Diff. ....	-0.02	$\pm 0.00$	+0.01	-0.01	

It is noteworthy that the slopes of the  $v$ - $c$  curves are approximately constant at  $p_H$ 's above 4.3, but on the acid side of this value they increase more and more rapidly as the  $p_H$  decreases. It is possible from the limiting slope and the divergences of slope, to make rough estimates of  $k_a$  and  $k_m$  respectively, although, of course, the experi-

FIG. 3.



ments were not designed with the object of measuring those quantities, and are not of the most suitable kind for that purpose. It appears, however, that  $k_a$  and  $k_m$  are both of the order of a few units times  $10^{-5}$ .

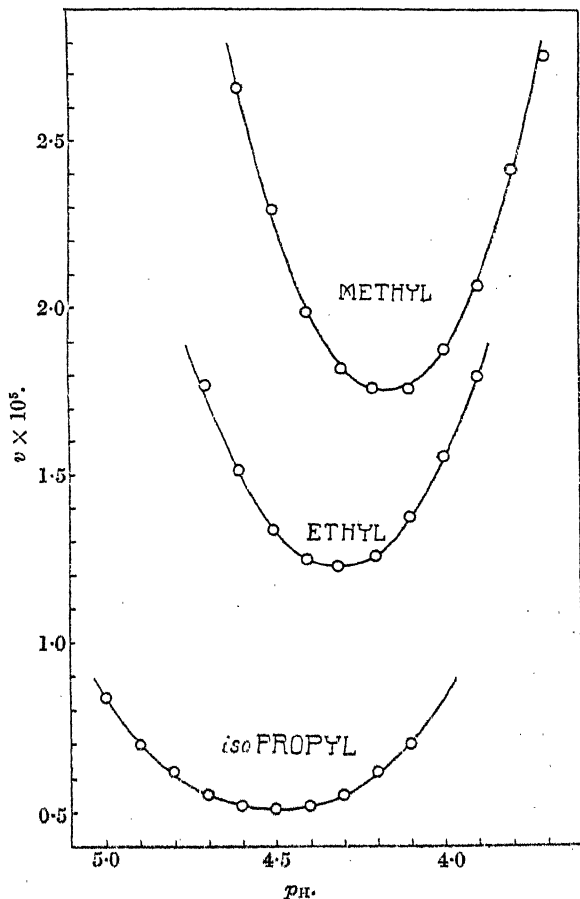
(E) *Short Summary of Results.*—The  $v$ - $p_H$  data ( $10^5 v$ ) for the esters and salt concentrations employed, obtained as illustrated in Sections C and D, are collected in Table VII. The extrapolated



velocity values ( $10^5 v_0$ ) for buffer-free solution are in Table VIII, and are shown graphically in Figs. 4 and 5.

The curves shown in conjunction with the  $v$ - $p_H$  data in Figs. 4 and 5 are graphs of equation (16) corresponding with certain assumed values of  $u_0$ ,  $h_0$ , and  $w_0$ . The assumed values of  $w_0$  are relatively

FIG. 4.



very small (of the order  $10^{-7}$ ) and the curves are not sensitive to their absolute magnitudes; conversely, the data shown in connexion with the curves do not enable the values of  $w_0$  to be fixed with any approach to precision. They do show, however, that the catalytic influence measured by  $w_0$ , viz., that of water molecules, is only of minor importance in the hydrolysis of carboxylic esters. We think

that Skrabal and Zahorka's claim (*Monatsh.*, 1929, **53**, **54**, 562) to have shown that 36% of the minimal velocity of hydrolysis of ethyl acetate at 25° is due to water catalysis is vitiated by the omission

FIG. 5.

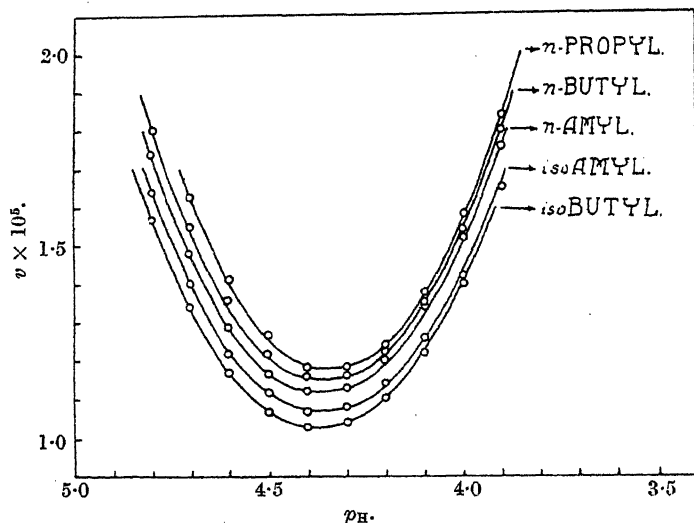


TABLE VIII.

Ester.	pH .....	5.0	4.9	4.8	4.7	4.6	4.5	4.4
Methyl .....	—	—	—	—	2.66	2.29	1.99	
Ethyl .....	—	—	—	1.77	1.52	1.34	1.25	
n-Propyl .....	—	—	—	1.64	1.42	1.27	1.18	
isoPropyl .....	0.84	0.70	0.62	0.55	0.52	0.51	0.52	
n-Butyl .....	—	—	1.80	1.55	1.36	1.22	1.16	
isoButyl .....	—	—	1.57	1.34	1.17	1.07	1.03	
n-Amyl .....	—	—	1.74	1.48	1.29	1.17	1.12	
isoAmyl .....	—	—	1.64	1.40	1.22	1.12	1.07	
Ester.	pH .....	4.3	4.2	4.1	4.0	3.9	3.8	3.7
Methyl .....	1.82	1.76	1.76	1.88	2.07	2.42	2.77	
Ethyl .....	1.23	1.26	1.38	1.56	1.80	—	—	
n-Propyl .....	1.18	1.24	1.38	1.58	1.82	—	—	
isoPropyl .....	0.55	0.62	0.70	—	—	—	—	
n-Butyl .....	1.16	1.22	1.35	1.53	1.80	—	—	
isoButyl .....	1.04	1.10	1.22	1.40	—	—	—	
n-Amyl .....	1.13	1.20	1.34	1.51	1.76	—	—	
isoAmyl .....	1.08	1.14	1.25	1.43	1.65	—	—	

to make allowance for buffer effects; probably the major portion of the percentage mentioned is to be laid to the account of the constituents of the buffers employed.

The values  $u_0$  and  $h_0$  correspond with the co-ordinates of the minima



of the curves. They are given in Table IX, together with the corresponding values of  $p_H^* = -\log_{10} h_0$ , and of  $k_{OH}/k_H = h_0^2/K_w$ . In the calculation of  $k_{OH}/k_H$  it is necessary to assume a figure for  $K_w$ , and  $10^{1.23-1.4}$  has been adopted as the result of interpolation from existing data. The value is inevitably arbitrary for the reason mentioned on p. 1045, but, as is there explained, there is reason to believe that its arbitrariness will not affect the purpose for which these measurements have been made.

TABLE IX.

Ester.	$u_0 \times 10^6$ .	$h_0 \times 10^6$ .	$p_H^*$ .	$(k_{OH}/k_H) \times 10^{-3}$ .
Methyl <i>dl</i> -glycerate .....	17.6	68.4	4.165	27.5
Ethyl " .....	12.3	47.9	4.320	13.5
<i>n</i> -Propyl " .....	11.8	44.7	4.350	11.8
<i>iso</i> Propyl " .....	5.1	31.3	4.505	5.8
<i>n</i> -Butyl " .....	11.5	44.2	4.355	11.5
<i>iso</i> Butyl " .....	10.3	42.7	4.370	10.7
<i>n</i> -Amyl " .....	11.2	43.7	4.360	11.2
<i>iso</i> Amyl " .....	10.7	43.7	4.360	11.2

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### CXXXI.—*The Anomalous Fifth Carbon Atom in n-Fatty Nitriles.*

By ROBERT AVERY FULTON and WILLIAM BELL LEE.

IN some series of straight-chain carbon compounds the 5th, 10th, and 15th members exhibit maxima or minima in many physical and chemical properties (Lee, *Trans. Faraday Soc.*, 1927, **23**, 79; Lee and van Rysselberge, *J. Physical Chem.*, 1929, **33**, 1543), and similar anomalies have been noted in molecular rotatory power by Pickard and Kenyon. Moreover, in homologous series of such compounds the alternation of physical properties between the odd and the even members is well known. Müller (*Proc. Roy. Soc.*, 1929, *A*, **124**, 317) postulates a plane, or nearly plane, zigzag structure of the carbon chain in such cases, but Henderson (*Proc. Roy. Soc. Edin.*, 1928, **48**, 20), from X-ray investigations of the dibasic acids of the oxalic acid series, concluded that the carbon chain was in spiral form.

The systematic and comparative experiments recorded below, which were made by one of us (R. A. F.) on six consecutive members of the series of nitriles of the *n*-fatty acids, demonstrate that a well-defined anomaly exists in the chemical reactions of the  $C_5$  nitrile. If a helicoidal configuration of the carbon atoms be assumed, every fifth carbon atom would correspond to one complete turn of the helix.

*Experiments in Liquid Ammonia Solution.*—Equimolecular quantities of the normal nitriles (from acetonitrile to hexonitrile) and of potassamide were electrolysed in liquid ammonia solution. The materials were carefully purified, and in all the experiments the conditions, *e.g.*, concentration, temperature ( $-33^{\circ}$ ), and current density (0.5 amp./sq. cm.), were kept as nearly as possible the same. The electrolysis was carried out in an apparatus similar to that used by Kolbe and others. The gases evolved in the reactions were analysed by low-temperature fractionation according to the method of Burrell (*U. S. Bureau of Mines Bulletin*, No. 104), and the analyses were accurate to approximately 0.1%.

Attention is focused entirely on the anode reactions, and the electrolysis is essentially that of the potassium salt of the "ammono"-fatty acid (Franklin; see *e.g.*, Cornell, *J. Amer. Chem. Soc.*, 1928, **50**, 3311) formed thus:  $\text{CH}_3\cdot\text{CN} + \text{KNH}_2 = \text{CH}_3\cdot\text{C}(\text{NH})\cdot\text{NHK}$ . Ammonocarbonic acid was always one of the products, and, except in the case of the ammonoacetate, hydrogen also was formed.

No. of C atoms in nitrile	2.	3.	4.	5.	6.
Methane, % .....	68.6	48.6	42.7	2.0	12.0
Ethane, % .....	None	None	None	70.5	50.0

The only variable in the different experiments was the length of the carbon chain. There is a definite "break" at the fifth carbon atom in the chemical reactions of these *n*-fatty nitriles. We assume that a stereochemical cause is responsible for this anomaly.

*Fusion of n-Fatty Nitriles with Potassamide.*—The nitriles were heated with potassamide in equimolecular quantity at  $350^{\circ}$ , the experiments being comparative. Again the only difference introduced was in the length of the chain.

No. of C atoms in nitrile.	2.	3.	4.	5.	6.
Gaseous products	$\text{CH}_4$	$\text{H}_2, \text{CH}_4$ $\text{C}_2\text{H}_6$	$\text{H}_2, \text{CH}_4$ $\text{C}_2\text{H}_6$ $\text{C}_3\text{H}_8$	$\text{CH}_4, \text{C}_3\text{H}_8$ , $\text{C}_4\text{H}_{10}$ ( $\text{C}_2\text{H}_6$ trace)	$\text{C}_2\text{H}_6, \text{C}_3\text{H}_8$ $\text{C}_4\text{H}_{10}$ ( $\text{CH}_4$ trace)

At  $\text{C}_5$  the yield of methane was a minimum with only a trace of ethane, whereas at  $\text{C}_6$  the ethane yield was good, with only a trace of methane. There is again a distinct anomaly at  $\text{C}_5$  in the reactions of these chemically similar nitriles. The mechanism of these reactions might be interpreted in different ways, and we lay less stress on these than on the electrolytic experiments. Nevertheless, there is some peculiarity which can be related to the number of carbon atoms in the chain.

Neither the ordinary plane formula of the organic chemist nor the plane zigzag of certain X-ray investigators accounts for this

chemical anomaly at the fifth carbon atom. The phenomenon is much more general than may have been supposed.

Our thanks are due to Professors E. C. Franklin and F. W. Bergstrom for their helpful suggestions during the course of this investigation.

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### CXXXII.—*The Addition of Halogens to Unsaturated Acids and Esters. Part III. The Velocity of Bromine-addition.*

By NORMAN WILLIAM HANSON and DAVID MATTHEW WILLIAMS.

WILLIAMS and JAMES (J., 1928, 343) showed that addition of bromine to unsaturated acids and esters in the dark in non-hydroxylic solvents, such as carbon tetrachloride and chloroform, was an autocatalytic reaction, and adduced evidence that the catalyst was hydrogen bromide. Davis (*J. Amer. Chem. Soc.*, 1928, 50, 2769) suggested that bromine-addition in the dark to olefins in carbon tetrachloride proceeded mainly through the medium of a bromine hydrate because the reaction velocity increased as the temperature was lowered from 25° to 0°. Further, the same thermal reaction was studied by Meyer and Pukall (*Z. physikal. Chem.*, 1929, 145, 360) for the case of cinnamic acid in chloroform; here, again, the reaction was autocatalytic, and it was suggested that the catalyst was produced by the action of bromine on the solvent and that the rapidity of the photobromination was due to the rapid production of the catalyst under the influence of light rays.

The present communication is an attempt to investigate systematically the effect of constitutional differences on the velocity of bromine-addition to unsaturated acids and methyl esters. The latter were used chiefly in those cases in which the acids were insoluble in the two solvents, and where comparison was possible, the ester was found to react slightly less readily than the acid. The addition was invariably more rapid in chloroform than in carbon tetrachloride, and hence, where choice was possible, the former was used for the slow and the latter for the rapid reactions. Solutions of purified bromine in either of the purified solvents can be kept in the dark for long periods without any deterioration, so the explanation of Meyer and Pukall does not seem to apply to the dark reaction.

The rate of addition to both forms of *o*-methoxycinnamic acid is

several hundred times greater than to cinnamic acid, the velocity diminishing more rapidly than would be expected for a bimolecular reaction (Williams and James, *loc. cit.*). This work has now been extended to include the methyl esters of *m*- and *p*-methoxycinnamic acids, and the reaction velocities are all of the same order of magnitude. The attachment of the strongly activating methoxyl group to the nucleus greatly intensifies the rate of nuclear substitution, and hence it seems that the enhanced rate of reaction is due to the ease with which hydrogen bromide is produced. This suggestion is in accordance with the observations of Davies and Davies (J., 1928, 602) and of Reimer and Tobin (*J. Amer. Chem. Soc.*, 1930, 52, 341), that addition of bromine respectively to *m*-methoxycinnamic acid and to 2:4-dimethoxycinnamic acid always results in considerable substitution in the nucleus. It was anticipated that a nuclear deactivating group directly attached to the nucleus in cinnamic acid would have the converse effect, decreasing the rate of addition and causing a long inhibition period. This expectation has been realised, for the nitro-group in the methyl esters of *o*-, *m*-, and *p*-nitrocinnamic acids was found to have the anticipated effects on the velocity of addition of bromine. Further, the inhibition periods vanished when hydrogen bromide was added initially as a catalyst.

Halogen atoms attached to the carbon atoms of the double linkage show interesting contrasts, for an  $\alpha$ -halogen atom completely inhibits addition, even in the presence of hydrogen bromide, while a  $\beta$ -halogen atom does not noticeably affect the rate. Although no other substituents in these positions have yet been studied, it is clear that the character of the groups attached to the doubly linked carbon atoms is an important factor in determining the rate.

Comparison of rates of addition to a number of *cis*- and *trans*-isomerides has shown that in every case addition of bromine to the *cis*-form occurs more readily, but the difference in rate varies considerably from pair to pair. An important fact relating to this point was discovered by the study of methyl fumarate and methyl maleate. Neither of these esters reacts with bromine in the dark in carbon tetrachloride at 18°. The fumarate is perfectly stable towards bromine even if heated in sealed tubes at 100° for several days, but the maleate is not so inactive at high temperatures: being an oil at ordinary temperature, it is more difficult to purify, and probably its impurities, by producing traces of hydrogen bromide, cause it to react slowly with bromine. In the presence of hydrogen bromide, the fumarate reacts with bromine very slowly, but the maleate reacts very rapidly and an apparent equilibrium is attained, after which the reaction is exceedingly slow. This is probably due to

the fact that a proportion of the maleate is converted into the fumarate under the influence of hydrogen bromide, concurrently with the addition. This shows that a third factor influencing the rate of addition is the rate of conversion of the unstable or *cis*-form into the stable or *trans*-form, and this seems to point to the existence of the same intermediate form in the conversion and in the addition. The same conclusion was reached by Schmidt (*Z. physikal. Chem.*, 1928, *B*, 1, 205) as regards the photochemical action of bromine on methyl maleate and methyl fumarate.

#### EXPERIMENTAL.

Exactly the same methods of purification of bromine and solvents were adopted as in the previous work. The solid esters were repeatedly recrystallised, and the liquid esters were twice redistilled under reduced pressure. The methyl maleate on standing for a few weeks deposited crystals of the fumarate, and since the presence of the latter does not interfere with the bromination of the former, a saturated solution of the fumarate in the maleate at 13° was used. This solution, as shown by the melting-point curve of mixtures of the two esters (Schmidt, *loc. cit.*), contains 4% of fumarate.

The procedure for the velocity measurements was modified accordingly as the reaction was rapid or slow. Equal volumes of *M*/30-solutions of the substance and of bromine at 0° were mixed either in well-stoppered brown bottles or in tubes, and the latter were at once sealed in a very faint red light. The vessels were then kept at 0° in the dark for the required period, the reaction being stopped either by adding excess of potassium iodide solution or by breaking the bulb under the solution. A definite volume (excess) of standard sodium thiosulphate solution was then added, the whole shaken until colourless, and the excess thiosulphate titrated against *N*/50-iodine solution.

In studying the catalytic effect of hydrogen bromide, definite volumes of a solution of the carefully dried gas in the solvent were added to the reaction mixture, a separate bottle being used for each determination. The concentration of the hydrogen bromide solution was determined either by titration with baryta or by precipitation as silver bromide. The catalytic effect on the addition of bromine to methyl maleate was so great that the best results were obtained by mixing 100 c.c. of each reacting solution in a large brown bottle, adding a definite volume of hydrogen bromide solution, and withdrawing samples of 20 c.c. for analysis at definite intervals.

The velocity measurements are summarised in the following tables. Since in no case was the reaction bimolecular in the absence of added hydrogen bromide, no velocity coefficients are given. For a com-

parison of rates, the approximate inhibition period and the time for 25% change are given, time being in hours throughout.

Table I shows the influence on the rate of the nitro- and methoxy-groups attached to the nucleus. The position of the substituent in the ring is a secondary factor compared with its nature. It will be seen that both types of addition, (a) and (b), are considerably accelerated by hydrogen bromide.

TABLE I.

Isomeride.	Without initial HBr.		With initial HBr.	
	Inhibition period.	Time for 25% change.	[HBr]/[Br <sub>2</sub> ].	Time for 25% change.
(a) Methyl nitrocinnamates. Solvent, CHCl <sub>3</sub> . Temp., 0°.				
ortho	ca. 60	750	0.758	155
meta	ca. 50	540	0.758	230
para	ca. 50	390	0.758	120
(b) Methyl methoxycinnamates. Solvent, CCl <sub>4</sub> . Temp., 0°.				
ortho	—	2.7	0.053	2.1
meta	—	21.0	0.432	0.22
para	—	0.1	0.204	0.01

In Table II are given the rates of addition to various pairs of *cis*- and *trans*-isomerides, including the  $\alpha$  and  $\beta$ -halogen-substituted cinnamic acids. The *cis*-acid is in every case the more reactive, and the effect of the position of the halogen atom is clearly indicated.

TABLE II.

Temperature, 0°.

Substance.	Solvent.	Inhibition period.	Time for 25% change.
<i>trans</i> -Cinnamic acid .....	CCl <sub>4</sub>	ca. 22	135
<i>cis</i> - " " .....	CCl <sub>4</sub>	ca. 7	35
<i>trans</i> - $\beta$ -Bromocinnamic acid .....	CHCl <sub>3</sub>	ca. 25	280
<i>cis</i> - " " .....	CHCl <sub>3</sub>	ca. 5	250
<i>trans</i> - $\beta$ -Chlorocinnamic acid .....	CHCl <sub>3</sub>	ca. 25	200
<i>cis</i> - " " .....	CHCl <sub>3</sub>	ca. 4	210
<i>trans</i> - $\alpha$ -Methoxycinnamic acid .....	CHCl <sub>3</sub>	—	0.05
<i>cis</i> - " " .....	CHCl <sub>3</sub>	—	0.02
Methyl <i>trans</i> - $\alpha$ -methoxycinnamate ...	CCl <sub>4</sub>	—	2.1
Methyl <i>cis</i> - " " .....	CCl <sub>4</sub>	—	0.40
$\alpha$ -Bromocinnamic acid (both forms) $\alpha$ -Chlorocinnamic acid (both forms) $\alpha\beta$ -Dibromocinnamic acid (both forms) $\beta$ -Chloro- $\alpha$ -bromocinnamic acid (both forms)			
Do not react to a measurable extent with bromine at 0° in either solvent, even under the influence of hydrogen bromide.			

The velocity measurements with methyl maleate and methyl fumarate were conducted in carbon tetrachloride in a thermostat at 18°. No addition took place to either of the esters unless hydrogen bromide was added, whereupon the two esters exhibited widely

different rates of reaction. In Table III are given the periods for 50% change with the maleate for different amounts of the catalyst, and also the position of equilibrium, which shows the percentage change into the fumarate.

TABLE III.

Solvent,  $\text{CCl}_4$ . Temp.,  $18^\circ$ .

(a) Methyl maleate.

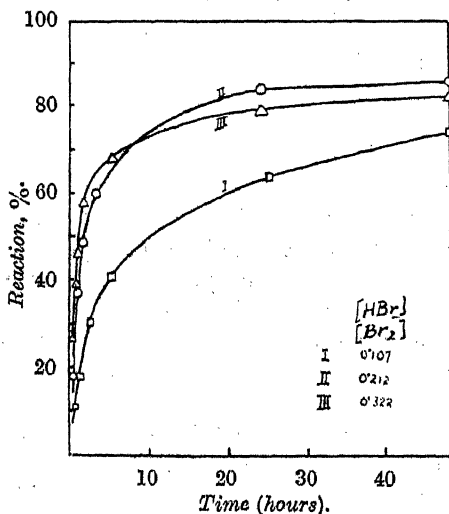
$[\text{HBr}]/[\text{Br}_2]$ .	Time for 50% change.	Percentage change at equilibrium.
0.107	9.5	—
0.212	1.6	85.4
0.322	0.95	81.5

(b) Methyl fumarate.

0.52                      9% of the bromine had reacted in 400 hours.

The actual figures obtained for the maleate are plotted in Fig. 1, in which it is shown that when the concentration of the catalyst is small, the reaction reaches an equilibrium very slowly.

FIG. 1.



Our best thanks are due to Professor T. C. James for valuable suggestions and criticism during this investigation. One of us (N. W. H.) desires to record his indebtedness to the Department of Scientific and Industrial Research for a maintenance grant.

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### CXXXIII.—*The Behaviour of Hydrogen Chloride in Different Solvents.*

By W. F. KENRICK WYNNE-JONES.

HYDROGEN chloride when dissolved in water behaves as a very strong electrolyte, so strong, indeed, that it is usual to regard it as a completely ionised acid, since its solutions conform quite closely to the equations of the Debye-Hückel theory. The anhydrous compound, on the other hand, is a non-electrolyte, and it is generally considered that the hydrogen and chlorine atoms are so intimately bound that it requires considerable energy to separate them as ions. These facts have led to the hypothesis that the dissociation of the acid is occasioned by its combination with the solvent and that, according to Brönsted's definition of an acid and a base (*Rec. trav. chim.*, 1923, **42**, 718), the acid will be ionised only in a basic solvent. Thus in water, ammonia, and methyl alcohol we have the reaction schemes  $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}'$ ;  $\text{HCl} + \text{NH}_3 \rightleftharpoons \text{NH}_4^+ + \text{Cl}'$ ;  $\text{HCl} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OH}_2^+ + \text{Cl}'$ .

This hypothesis makes a clear distinction between an electrolyte such as hydrochloric acid and other strong electrolytes such as salts, since, with the latter, dissociation is primarily determined by the dielectric constant, whereas with hydrochloric acid the chemical nature of the medium is the determining factor.

In order to test this hypothesis further, it was decided to examine the behaviour of hydrogen chloride in a solvent of no marked basic character but possessing a fairly high dielectric constant. For this purpose, nitrobenzene seemed admirably suited, since its dielectric constant is 34, and, from an acid-base standpoint, it might be expected to be inert; moreover its immiscibility with water made it possible to use the partition method for investigating the behaviour of hydrogen chloride.

This method has been employed by several investigators, and the work of Rothmund and Drucker (*Z. physikal. Chem.*, 1903, **46**, 827) and of Cavanagh (*Proc. Roy. Soc.*, 1924, *A*, **106**, 243), in particular, has proved the trustworthiness of the method for determining activities in one solvent when those in the other solvent are known. There has, however, been a certain amount of criticism of the method, owing partly to a misunderstanding of the nature of the results obtained by it, and partly to a misconception of its limitations. On the one hand, it is clear that the Nernst equation

$$K = C_1^n / C_2 \quad \dots \quad (1)$$

where  $C_1$  and  $C_2$  refer to the concentrations in the two solvents and  $n$  is the degree of association in solvent 2, is only an approximation



and certainly cannot hold for electrolytes. A more precise method of treating the results is to write for solutions in one solvent

$$\mu = RT/n \cdot \log cf + k \quad (2)$$

where  $\mu$  is the chemical potential of the solute,  $n$  the degree of association,  $f$  the activity coefficient of the associated molecules, and  $k$  a constant, the other symbols having the usual significance. If, for the other solvent, the values of  $\mu$  are known, then these values may be substituted in the above equation. In a case such as that studied here, we may write for aqueous solutions

$$\mu_1 = RT \log p + k_1 \quad (2a)$$

while for solutions in nitrobenzene we have

$$\mu_2 = RT/n \cdot \log cf + k_2 \quad (2b)$$

whence, for equilibrium,

$$K = p^n/cf \quad (3)$$

$p$  being the partial pressure.

The limitations of the method, on the other hand, must be clearly recognised. Evidently, the application of equation (2a) is only justifiable if the chemical potential of the solute is not markedly affected by the presence of the other solvent. Also the results for the second solvent will refer, not to the pure liquid, but to one saturated with the other solvent. The solubility of one solvent in the other, provided it remain constant, as at low concentration of the solute, will not invalidate the results; if, however, the solubility varies appreciably, then some uncertainty will be introduced dependent upon the manner in which the potential of the solute varies with the properties of the solvent.

#### EXPERIMENTAL.

In view of the fact that hydrogen chloride is much more soluble in water than in nitrobenzene, it was thought possible that errors might arise through traces of emulsification if the two liquids were brought into direct contact as is usual in partition measurements. In order to avoid this, an H form of apparatus was constructed and equilibrium between the two liquids was reached through the vapour phase; the attainment of equilibrium was accelerated by evacuating the apparatus through a tap on the connecting tube. Siphon tubes were introduced through rubber stoppers in the two upright tubes, and the apparatus was filled and emptied by means of these siphons. In most of the experiments the apparatus was left in a thermostat, electrically controlled at  $25.00^\circ \pm 0.01^\circ$ , for 2—5 days with occasional shaking; in a few of the later experiments a shaking apparatus was installed and equilibrium attained

in less than 24 hours. At the end of this time air was admitted to the apparatus, the ends of the siphons were broken, and suitable amounts of the two liquids run into flasks and weighed. Titrations were carried out with carbonate-free sodium hydroxide, bromocresol-purple being used as indicator. The ultimate standard was constant-boiling hydrochloric acid, prepared according to the directions of Foulk and Hollingsworth (*J. Amer. Chem. Soc.*, 1923, **45**, 1220).

In one experiment with nitrobenzene and all the experiments with benzene the two liquids were shaken together in stoppered bottles. The agreement of the nitrobenzene value thus obtained with the others is satisfactory evidence that either method can give correct results under proper conditions.

The solubility of hydrogen chloride in water and nitrobenzene was determined by passing the gas for several hours through the liquids contained in test tubes: the gas passed out through two guard tubes and was then absorbed in alkali. The hydrogen chloride was generated by dropping A.R. hydrochloric acid into concentrated sulphuric acid. As a check on this method, a few measurements were made with gas generated by the action of sulphuric acid on ammonium chloride, but no difference was detected.

The nitrobenzene was of "pure" quality. It was shaken with caustic soda and distilled twice under 20 mm. pressure, the second distillation being from phosphoric oxide. The final product was very pale yellow.

*Results.*—The results are summarised in Table I. In the first column are recorded the values ( $C_w$ ) of the concentration in the

TABLE I.  
Results for nitrobenzene at 25°.

$C_w$	$C_n$	$\alpha_{HCl} \times 10^{-5}$	$C_w$	$C_n$	$\alpha_{HCl} \times 10^{-5}$	$C_w$	$C_n$	$\alpha_{HCl} \times 10^{-5}$
9.635	0.0027	0.0828	14.84	0.0707	2.37	18.05	0.335	11.9
9.766	0.0029	0.0912	14.93	0.0773	2.77	18.38	0.394	13.4
11.147	0.0080	0.242	15.21	0.0833	2.93	†19.33	0.556	18.8
*11.61	0.0109	0.331	16.46	0.164	5.70	19.52	0.603	20.5
12.84	0.0229	0.721	17.19	0.223	8.28	20.42	0.833	27.3
13.84	0.0396	1.33	17.76	0.292	10.6			

\* This value was obtained from an experiment in a stoppered bottle.

† This value is obtained from the following determinations of the solubility of hydrogen chloride in the two solvents:

	$p_{HCl}$ (mm. Hg).	$C$ .	$C$ (corr. to 760 mm.).
Water	747	19.29	19.34
	752	19.29	19.32
			Mean 19.33
Nitrobenzene (saturated with water)	742	0.535	0.548
	749	0.551	0.559
	760	0.561	0.561
			Mean 0.556

aqueous layer expressed in mols. per 1000 g. of water; in the 2nd, the concentrations ( $C_n$ ) in the nitrobenzene similarly expressed; in the 3rd, the values of the activities in the aqueous layer calculated from the data of Randall and Young (*J. Amer. Chem. Soc.*, 1928, 50, 989) up to a concentration of 16 molal, and, for higher concentrations, from the vapour pressures given in the International Critical Tables, Vol. III, p. 301.

### *Discussion of Results.*

On comparing these results with those of Knight and Hinshelwood (*J.*, 1927, 470) for the distribution of hydrogen chloride between benzene and water, we find two marked differences. In the first place, there is a difference in the general form of the curves representing the variation of the concentration in the non-aqueous phase with the concentration in the water. For, whereas in this work the curve rises continuously and is always concave towards the axis of the concentration in the water, Knight and Hinshelwood's curve has a point of inflexion and flattens out very considerably at high concentrations, where a constant value is actually obtained for the ratio of the concentrations in the two layers. Such a result is quite inexplicable on theoretical grounds and, moreover, is in conflict with the vapour-pressure data of a number of authors. That it is probably due to some experimental error is further shown by the fact that the value given by Knight and Hinshelwood for the solubility of hydrogen chloride in water at 20° differs considerably from the standard value. Thus, Roscoe and Dittmar (*J.*, 1859, 12, 128) found that 1 g. of water at 20° dissolves 0.721 g. of hydrogen chloride, whereas Knight and Hinshelwood found that 1 litre of the saturated solution contains 718.8 g. of hydrogen chloride; combining this with the density of the solution, *viz.*, 1.22, we obtain a value of 1.44 g. of hydrogen chloride per g. of water.

TABLE II.

Knight and Hinshelwood's results at 20°.

$C_w$ , g./l.	$C_b$ , g./l.	$p_{HCl}$	$p_{HCl}/C_b$
165.9	0.100	0.0343	0.343
212.0	0.252	0.162	0.643
236.1	0.382	0.351	0.92
249.0	0.449	0.538	1.20
259.0	0.532	0.742	1.40
289.3	0.706	1.905	2.70
312.0	0.929	3.91	4.21

A further peculiarity about the results of these authors is that the concentrations in the benzene layer are not even approximately proportional to the partial pressures of the aqueous solutions. This is shown in Table II where a few of the data are tabulated.

The concentrations are expressed as g. of acid per litre of solution; the vapour pressures have been interpolated from the data in the International Critical Tables (*loc. cit.*) and are expressed in mm. of mercury.

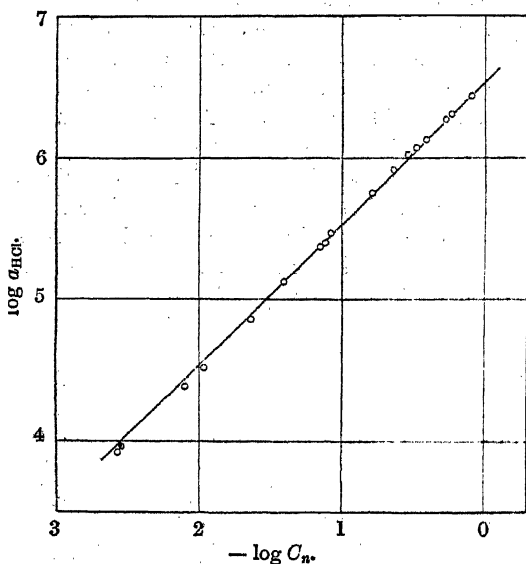
In order to determine whether this deviation from normality had any real existence, it was decided to carry out a few experiments with benzene. The results are summarised in Table III, in which the concentrations are expressed as mols. per 1000 g. of solvent.

TABLE III.  
Results with benzene at 25°.

$C_w$	$C_b$	$p_{\text{HCl}}$	$p_{\text{HCl}}/C_b \times 10^3$
9.603	0.00213	2.95	1.39
10.215	0.00340	4.67	1.37
10.508	0.00423	5.72	1.35
11.43	0.00768	10.74	1.40
11.99	0.0110	15.6	1.42
12.93	0.0216	28.1	1.30

It is clear that the behaviour of hydrogen chloride in benzene is quite normal.

FIG. 1.



That hydrogen chloride is a normal solute in nitrobenzene also is shown most clearly in Fig. 1, where the logarithm of the activity is plotted against the logarithm of the concentration in the solvent; the straight line has been drawn with a slope of unity and it is

evident that over the whole range the activity is proportional to the concentration.

As previously mentioned, the activities were obtained by combining Randall and Young's results with the vapour-pressure data in the International Critical Tables. If Randall and Young's values of  $\log \gamma$  are plotted against  $\sqrt{M}$  (where  $M$  = molality) a linear relationship holds over the range 9–16*M*, but it is not possible to use this for extrapolation, since the values thus obtained diverge considerably from the values calculated from the vapour pressures by means of the equation

$$\log \gamma - 1.718 = \log \sqrt{p}/M.$$

That there is no serious error in the vapour pressures is shown by the fact that the interpolated value for the concentration of the saturated solution (under a pressure of 760 mm. of Hg) is 19.33*M*, in exact agreement with the figure obtained in this work. It is also quite justifiable to calculate activities from the vapour pressures, since Gray and Burt (J., 1909, 95, 1633) have shown that at 0° and a pressure of 1 atm. the deviation of hydrogen chloride vapour from the gas laws is less than 1%. Since there are no published values for the activity coefficients of hydrochloric acid at concentrations above 16*M*, Table IV has been compiled from the vapour-pressure data.

TABLE IV.

Activity coefficients of hydrochloric acid at 25°.

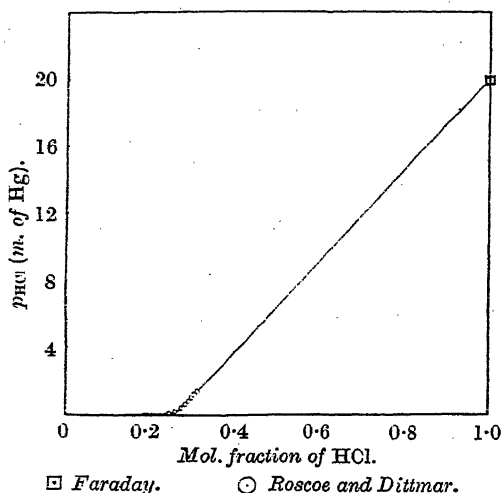
<i>M</i> (mols./1000 g.) ...	16	17	18	19	20
$\log \gamma$ .....	1.628	1.708	1.776	1.836	1.890
<i>p</i> (mm. Hg) .....	169.1	276	423	623	884

The value of  $\log \gamma$  at 16*M* is that given by Randall and Young and may be somewhat in error, but further investigation is required to decide this.

The results presented in this paper clearly support the theoretical considerations outlined in the introduction: in the three solvents water, nitrobenzene, and benzene, with dielectric constants 79, 34, and 2.2, respectively, the behaviour of hydrogen chloride is conditioned, not by the dielectric constant of the medium, but by its capacity to combine with it. That hydrogen chloride probably forms a compound with water has long been postulated, but it is interesting to note that vapour-pressure data lend considerable support to this view and also enable us, on the basis of a simple assumption, approximately to evaluate the extent of combination. Roscoe and Dittmar have measured the vapour pressures of hydrochloric acid solutions at 0° up to a pressure of 1300 mm.; in addition, Faraday (*Phil. Trans.*, 1845, 135, 155) determined the vapour

pressure of pure hydrogen chloride at the same temperature. These results are combined in Fig. 2, where the vapour pressure is plotted against the mol fraction of hydrogen chloride, which is calculated on the assumption that the molecular weights of hydrogen chloride and of water are normal. Although there is a large range for which no data are available, it is very striking that a linear extrapolation of Roscoe and Dittmar's results comes very close to Faraday's value for pure hydrogen chloride. The whole form of the curve strongly suggests that at mol fractions of less than 0.25 practically all the hydrogen chloride has combined with the water and exerts a negligible vapour pressure, whereas above that value any additional hydrogen chloride added to the solution is uncombined and is able

FIG. 2.



to exert its full vapour pressure. This can be simply explained if each molecule of hydrogen chloride is combined with 3 molecules of water.

If we now assume that the partial pressure of hydrochloric acid is always proportional to the mol fraction of the uncombined acid, it is possible to calculate its amount. Thus, the partial pressure of a molal solution at  $0^\circ$  is  $2 \times 10^{-8}$  atm., while the vapour pressure of pure hydrogen chloride is 26.2 atm.; hence the mol fraction of uncombined hydrochloric acid is  $2 \times 10^{-8}/26.2$ , and its molality is  $55 \times 2 \times 10^{-8}/26.2 = 4 \times 10^{-8}$ . On the assumption that all the combined hydrogen chloride is ionised, the dissociation constant of hydrochloric acid is  $K = 1/4 \times 10^{-8} = 2.5 \times 10^7$ . This value agrees well with the previous estimates of Schreiner (*Z. physikal.*

*Chem.*, 1924, **111**, 419) and of Ebert (*Naturwiss.*, 1925, **13**, 393), both based on quite different considerations.

*Summary.*

The partition of hydrogen chloride between nitrobenzene and water has been determined, and the results indicate that in nitrobenzene it behaves as a normal undissociated solute. A few measurements on the system benzene-water lead to a similar conclusion. These results support the view that the behaviour of an acid is primarily determined by the basic character, and not by the dielectric constant, of the solvent.

Consideration of the vapour-pressure data shows that a molecule of hydrogen chloride in aqueous solution is probably associated with 3 molecules of water, and it is estimated that the dissociation constant of hydrochloric acid is  $2.5 \times 10^7$ .

I wish to express my thanks for a grant from the Research Fund of the Chemical Society which has helped to defray the cost of this work.

THE UNIVERSITY, READING.

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# CXXXIV.—*Investigations in the Diphenyl Series. Part IX. Further Experiments with Sulphonamides.*

By FRANK BELL.

ALTHOUGH the acetyl derivatives of 2-amino- and 4-amino-diphenyl can be nitrated only to dinitro-compounds (Scarborough and Waters, J., 1927, 89), it appeared probable that by the use of sulphonyl derivatives trinitro-compounds and hence trinitroamines would be obtainable (Bell, J., 1928, 2772). To avoid complications during the vigorous nitration, *m*-nitrobenzenesulphonyl derivatives were employed and in this way both 2-amino- and 4-amino-diphenyl were easily converted into trinitro-compounds.

The reaction of outstanding interest in the substitution of derivatives of 2-amino- and 4-amino-diphenyl is the bromination of 4-acetamidodiphenyl (Scarborough and Waters, J., 1926, 507; Kenyon and Robinson, *ibid.*, p. 3050), for in marked contrast with every other simple monosubstitution reaction of aminodiphenyls and their derivatives there is produced a considerable yield of a heteronuclear-substituted product, 4'-bromo-4-acetamidodiphenyl.

Since the above experiments showed that the arylsulphonamides readily undergo substitution, the bromination of 2- and 4-*p*-toluenesulphonamidodiphenyls was investigated. The latter is brominated

exclusively in the 3-position and is then dibrominated in the 4'-position, whereas 2-*p*-toluenesulphonamidodiphenyl is brominated in the 5-position and is then resistant to further substitution under the conditions employed.

These results show very clearly the marked difference which exists in the processes of nitration and bromination. Both 2- and 4-*p*-toluenesulphonamidodiphenyls are dinitrated with the utmost ease in the 3 : 5-positions and although the failure to brominate 3-bromo-4-*p*-toluenesulphonamidodiphenyl in the 5-position may be attributed to the competitive action of the bromo- and the *p*-toluenesulphonamido-group acting in the same nucleus, this explanation can scarcely be valid for the monobromination of 4-acetamidodiphenyl.

The comparison of the processes of nitration and bromination was extended to include 4-methoxydiphenyl. This substance on bromination gave a mixture of 3-bromo- and 4'-bromo-4-methoxydiphenyls, the yields being about 60% and 30% respectively. Both these monobromo-derivatives on further bromination gave 3 : 4'-dibromo-4-methoxydiphenyl. In this case, therefore, there is much less contrast between bromination and nitration (Bell and Kenyon, J., 1926, 3047).

It was intended to include 2-dimethylaminodiphenyl in this study, but 2-aminodiphenyl on methylation under the same conditions which readily produced 4-dimethylaminodiphenyl (Bell, J., 1926, 2709) gave only 2-methylaminodiphenyl.

During the course of this work it was noticed that certain of these sulphonamides readily reacted with a further molecule of sulphonyl chloride to give disulphonamides, and it was thought of interest to examine this reaction in greater detail. The following results were obtained :

(a) 3 : 5-Dibromo-4-aminodiphenyl, 2-nitro-*p*-toluidine, and 6-nitro-*o*-toluidine reacted with the sulphonyl chloride (1 mol.) to give disulphonamides. The yield was not quantitative even when 2 mols. of sulphonyl chloride were employed, and therefore the velocity of disulphonamide formation must be high compared with that of monosulphonamide formation.

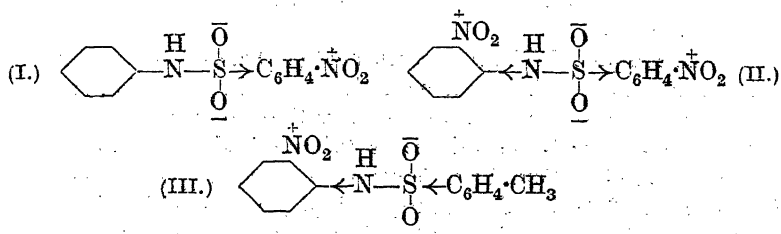
(b) *o*-Nitroaniline and 1 : 8-dinitro- $\beta$ -naphthylamine with the sulphonyl chloride (1 mol.) gave mixtures of monosulphonamide and disulphonamide (Bell, J., 1929, 2787).

(c) Other amines gave monosulphonamides which were converted into disulphonamides with very different velocities.

It would appear that the velocity of disulphonamide formation is determined by the tendency of the sulphonamide-hydrogen atom to undergo ionisation. For instance, the *m*-nitrobenzenesulphonyl derivatives of the nitroanilines (II) react readily with a molecule of a



sulphonyl chloride, whereas that of aniline (I) reacts very slowly. This accords with the electron-absorbing character of the nitro-group, which is most easily satisfied if the hydrogen of the amino-group



separates with a positive charge (gives up its electron and separates as a hydrogen ion). Similarly the mobility of this hydrogen atom is influenced by the substituents present in the benzenesulphonyl group. It would be expected that *p*-toluenesulphonamides (III) should be less reactive than *m*-nitrobenzenesulphonamides, and this is actually the case. For example, under the same experimental conditions, *m*-nitrobenzenesulphon-*m'*-nitroanilide reacts quantitatively with *p*-toluenesulphonyl chloride, whereas *p*-toluenesulphon-*m'*-nitroanilide gives only a 50% yield of the same compound when treated with *m*-nitrobenzenesulphonyl chloride.

Sulphonamides capable of giving rise to disulphonamides will also undergo acetylation. For instance, *p*-toluenesulphon-*m'*-nitroanilide is easily converted into *p*-toluenesulphon-*m'*-nitroacetanilide. On the other hand, the acetyl derivatives of *o*- and *m*-nitroanilines did not react with either *m*-nitrobenzenesulphonyl chloride or *p*-toluenesulphonyl chloride in pyridine solution. This is comparable with the well-known fact that secondary amines, such as methyl-aniline, are readily acetylated, whereas acetylated primary amines cannot be methylated by shaking with methyl sulphate.

The diminution in directing power which takes place when the sulphonamido- is converted into the disulphonamido-group (J., 1929, 2877) is further illustrated by the fact that 5-nitro-2-di-*m*-nitrobenzenesulphonamidodiphenyl can only be converted into a dinitro-derivative, whereas the sulphonamido-derivative is easily trinitrated. Also *m*-nitrobenzenesulphon-*m'*-nitroanilide is very vigorously attacked by fuming nitric acid, whereas di-*m*-nitrobenzenesulphon-*m*-nitroanilide can be recovered unchanged from this reagent.

#### EXPERIMENTAL.

Unless otherwise stated, sulphonamides and disulphonamides were prepared by interaction of the appropriate amine, or sulphonamide,

and sulphonyl chloride in pyridine solution and were recrystallised from acetic acid.

4-m-Nitrobenzenesulphonamidodiphenyl formed colourless needles, m. p.  $149^{\circ}$  (Found: C, 61.3; H, 4.0.  $C_{18}H_{14}O_4N_2S$  requires C, 61.0; H, 4.0%).

To this compound (15 g.) in acetic acid (150 c.c.) was added nitric acid ( $d$  1.5, 15 c.c.) in acetic acid (15 c.c.). The solution rapidly deposited crystals which, after recrystallisation from acetic acid, gave pure 3-nitro-4-m-nitrobenzenesulphonamidodiphenyl in yellow prisms, m. p.  $170^{\circ}$  (Found: C, 54.2; H, 3.3.  $C_{18}H_{13}O_6N_3S$  requires C, 54.1; H, 3.3%). This compound (5 g.) was added in small portions to nitric acid ( $d$  1.5, 12 c.c.) and after  $\frac{1}{4}$  hour the resultant solution was diluted with acetic acid; the 3:5:4'-trinitro-4-m-nitrobenzenesulphonamidodiphenyl thus precipitated, after crystallisation from acetic acid, formed needles, m. p.  $199^{\circ}$  (Found: C, 44.2; H, 2.3.  $C_{18}H_{11}O_{10}N_5S$  requires C, 44.2; H, 2.3%). 3 G. were dissolved in sulphuric acid (6 c.c.) and after  $\frac{1}{4}$  hour the solution was poured into water. The resulting precipitate after crystallisation from pyridine gave 3:5:4'-trinitro-4-aminodiphenyl as long yellow needles, m. p.  $282^{\circ}$  (Found: C, 46.9; H, 2.6.  $C_{12}H_8O_6N_4$  requires C, 47.4; H, 2.6%).

3-Nitro-4-di-m-nitrobenzenesulphonamidodiphenyl formed prisms, m. p.  $187^{\circ}$  (Found: C, 48.8; H, 2.8.  $C_{24}H_{16}O_{10}N_4S_2$  requires C, 49.3; H, 2.7%), and 2-m-nitrobenzenesulphonamidodiphenyl colourless needles, m. p.  $128^{\circ}$  (Found: C, 61.0; H, 4.1.  $C_{18}H_{14}O_4N_2S$  requires C, 61.0; H, 4.0%).

Nitration of 2-m-Nitrobenzenesulphonamidodiphenyl.—(a) 3 G. were warmed on a water-bath for 15 hours with a mixture of water (20 c.c.) and nitric acid (4 c.c.). The product, crystallised from alcohol, gave 5-nitro-2-m-nitrobenzenesulphonamidodiphenyl in platelets, m. p.  $150^{\circ}$  (Found: C, 54.3; H, 3.5.  $C_{18}H_{13}O_6N_3S$  requires C, 54.1; H, 3.3%).

(b) To 4 g., dissolved in acetic acid (40 c.c.) at  $70^{\circ}$ , was added nitric acid ( $d$  1.5; 3 c.c.) in acetic acid (3 c.c.) and the whole was maintained at  $70^{\circ}$  for  $\frac{1}{4}$  hour. On cooling, the liquid filled with pale yellow leaflets, m. p. *ca.*  $145^{\circ}$ , containing acetic acid of crystallisation. Recrystallised from alcohol, this product furnished pure 3:5-dinitro-2-m-nitrobenzenesulphonamidodiphenyl in needles, m. p.  $148^{\circ}$  (Found: C, 48.2; H, 2.9.  $C_{18}H_{12}O_8N_4S$  requires C, 48.7; H, 2.7%). This constitution was proved by hydrolysis: a solution of the compound (1 g.) in sulphuric acid (2 c.c.) was after  $\frac{1}{2}$  hour poured into water and neutralised with ammonia; the precipitated 3:5-dinitro-2-aminodiphenyl crystallised from alcohol in yellow plates, m. p.  $182^{\circ}$  (Bell, J., 1928, 2774).

(c) 3 : 5-Dinitro-2-*m*-nitrobenzenesulphonamidodiphenyl (2 g.) was added slowly to nitric acid (*d* 1.5; 6 c.c.), and the solution poured into water. The resulting gum was filtered off, dried, and crystallised from benzene. After benzene had been expelled by heating at 120° for several hours, impure 3 : 5 : 4'-*trinitro*-2-*m*-nitrobenzenesulphonamidodiphenyl was obtained as a pale yellow powder, m. p. 170—175° (Found : C, 44.9; H, 2.6.  $C_{18}H_{11}O_{10}N_3S$  requires C, 44.2; H, 2.3%). Hydrolysis of this gave 3 : 5 : 4'-*trinitro*-2-aminodiphenyl as prisms, m. p. 239° after recrystallisation from pyridine (Bell, J., 1928, 2775).

5-Nitro-2-*di-m*-nitrobenzenesulphonamidodiphenyl was obtained as a white powder, m. p. 222° (Found : C, 49.5; H, 2.9.  $C_{24}H_{16}O_{10}N_4S_2$  requires C, 49.3; H, 2.7%).

This compound (2 g.) was added to nitric acid (*d* 1.5; 5 c.c.); after  $\frac{1}{4}$  hour the solution was diluted with acetic acid, and the resulting precipitate collected and extracted with hot acetic acid; 5 : 4' (?) -*dinitro*-2-*di-m*-nitrobenzenesulphonamidodiphenyl, m. p. 240°, was left undissolved (Found : C, 45.4; H, 2.7.  $C_{24}H_{15}O_{12}N_5S_2$  requires C, 45.8; H, 2.4%). Attempts to hydrolyse this compound were unsuccessful.

*Bromination of 4-Methoxydiphenyl.*—To 4-methoxydiphenyl (8 g.) in chloroform (25 c.c.) was added bromine (7 g.) in chloroform (10 c.c.). The solution was evaporated, and the residue fractionally crystallised from petroleum; it then separated into 4'-*bromo*-4-methoxydiphenyl, plates, m. p. 144° (Found : C, 59.2; H, 4.0.  $C_{13}H_{11}OBr$  requires C, 59.3; H, 4.2%), and the more soluble 3-*bromo*-4-methoxydiphenyl, large prismatic needles, m. p. 79° (Found : C, 59.6; H, 4.4%). Both compounds were identified by comparison with the products obtained by the methylation of the corresponding bromo-4-hydroxydiphenyls.

3 : 4'-*Dibromo*-4-methoxydiphenyl.—(a) To a warm solution of 4'-*bromo*-4-methoxydiphenyl in chloroform was added bromine (1 mol.) in chloroform. The mixed solution was evaporated to small bulk and diluted with petroleum; 3 : 4'-*dibromo*-4-methoxydiphenyl, m. p. 134°, then separated.

(b) 3-Bromo-4-methoxydiphenyl treated as under (a) gave a product from which a 60% yield of purified 3 : 4'-*dibromo*-4-methoxydiphenyl was obtained (Found : C, 45.8; H, 2.9.  $C_{13}H_{10}OBr_2$  requires C, 45.5; H, 2.9%).

3 : 5-*Dibromo*-4-methoxydiphenyl, prepared by methylation of the corresponding phenol, crystallised from petroleum in needles, m. p. 87° (Found : C, 45.2; H, 2.7%).

3 : 5 : 4'-*Tribromo*-4-methoxydiphenyl, prepared by methylation of the corresponding phenol, crystallised from benzene in needles, m. p.

115° (Found: C, 36.7; H, 2.2.  $C_{13}H_{19}OBr_3$  requires C, 36.9; H, 2.1%).

*Dibromination of 4-p-Toluenesulphonamidodiphenyl.*—To 7 g. in warm chloroform (20 c.c.) was added bromine (7.5 g.) in chloroform (3 c.c.). The reaction was completed on the water-bath and after cooling the solution was filtered from the hydrobromide of 3:5:4'-tribromo-4-aminodiphenyl (free base, m. p. 149°; acetyl derivative, m. p. 256°). The filtrate on concentration deposited large prismatic needles containing chloroform of crystallisation (loss in weight on drying at 100° = 15.3%), which on recrystallisation from alcohol furnished pure 3:4'-dibromo-4-p-toluenesulphonamidodiphenyl in prisms, m. p. 130° (Found: C, 47.1; H, 3.1.  $C_{19}H_{13}O_2NBr_2S$  requires C, 47.4; H, 3.1%).

*Bromination of 4'-Bromo-4-p-toluenesulphonamidodiphenyl.*—To 5 g. in warm chloroform (20 c.c.) was added bromine (2 g.) in chloroform (3 c.c.). Treated as above, this gave a small amount of 3:5:4'-tribromo-4-aminodiphenyl hydrobromide, the remainder being almost pure 3:4'-dibromo-4-p-toluenesulphonamidodiphenyl.

3:4'-Dibromo-4-di-p-toluenesulphonamidodiphenyl formed needles, m. p. 238° (Found: C, 49.1; H, 3.3.  $C_{26}H_{21}O_4NBr_2S_2$  requires C, 49.1; H, 3.3%).

3:5-Dibromo-4-di-p-toluenesulphonamidodiphenyl, the only product which could be isolated from the interaction of 3:5-dibromo-4-p-toluenesulphonamidodiphenyl and p-toluenesulphonyl chloride (1 mol.) in pyridine solution, crystallised from pyridine in needles, m. p. 291° (Found: C, 49.5; H, 3.3%).

*Bromination of 2-p-Toluenesulphonamidodiphenyl.*—To 10 g. in chloroform (30 c.c.) was added bromine (5 g.) in chloroform (5 c.c.). After completion of the reaction the solution was evaporated to small bulk and diluted with light petroleum; 5-bromo-2-p-toluenesulphonamidodiphenyl then separated in almost theoretical yield. It was recrystallised from alcohol, forming stout needles, m. p. 115° (Found: C, 56.9; H, 4.0.  $C_{19}H_{16}O_2NBrS$  requires C, 56.7; H, 4.0%), and was identical with the compound obtained by the interaction of 5-bromo-2-aminodiphenyl (Scarborough and Waters, J., 1927, 94) and p-toluenesulphonyl chloride in pyridine solution.

Attempts to dibrominate 2-p-toluenesulphonamidodiphenyl resulted in the production of gummy masses containing 3:5-dibromo-2-aminodiphenyl (compare Scarborough and Waters, *loc. cit.*, p. 95).

*Methylation of 2-Aminodiphenyl.*—2-Aminodiphenyl was shaken with a considerable excess of methyl sulphate and sodium hydroxide, and the resultant oil extracted with ether. The ethereal extract was dried with sodium sulphate, evaporated, and the residue distilled in a vacuum. The distillate, b. p. 155°/10 mm., appeared to be a mixture

of substances, as it would not set solid. It was therefore dissolved in dilute hydrochloric acid and treated with a slight excess of sodium nitrite. The liquid was extracted with ether, the extract dried and evaporated, and the residue crystallised from alcohol. It gave stout prismatic needles of 2-nitrosomethylaminodiphenyl, m. p.  $70^{\circ}$  (Found: C, 73.7; H, 5.8.  $C_{13}H_{12}ON_2$  requires C, 73.6; H, 5.7%). From the aqueous layer left after the ether extraction, no substance corresponding in properties with a nitroso-tertiary base could be isolated.

*Acetylation of p-Toluenesulphon-m'-nitroanilide.*—This substance was dissolved in warm acetic anhydride and two drops of sulphuric acid were added. On cooling, p-toluenesulphon-m'-nitroacetanilide separated; it formed a white powder, m. p.  $165^{\circ}$ , after recrystallisation from acetic acid (Found: C, 54.2; H, 4.3.  $C_{15}H_{14}O_5N_2S$  requires C, 53.9; H, 4.2%).

By the same method m-nitrobenzenesulphon-p'-nitroanilide was converted into m-nitrobenzenesulphon-p'-nitroacetanilide, m. p.  $214^{\circ}$  (Found: C, 45.8; H, 3.4.  $C_{14}H_{11}O_7N_3S$  requires C, 46.0; H, 3.0%).

m-Nitrobenzenesulphon-m'-nitroanilide, prisms, m. p.  $151^{\circ}$  (Found: C, 44.9; H, 2.9.  $C_{12}H_9O_6N_3S$  requires C, 44.6; H, 2.8%), underwent vigorous nitration on dissolving in fuming nitric acid to give a mixture of polynitro-compounds.

Di-m-nitrobenzenesulphon-m'-nitroanilide, white powder, m. p.  $235^{\circ}$  (Found: C, 42.2; H, 2.6.  $C_{18}H_{12}O_{10}N_4S_2$  requires C, 42.5; H, 2.4%), was recovered unchanged after solution in fuming nitric acid.

m-Nitrobenzenesulphon-p-toluenesulphon-m'-nitroanilide, prepared by interaction of m-nitrobenzenesulphonyl chloride and p-toluenesulphon-m'-nitroanilide or of p-toluenesulphonyl chloride with m-nitrobenzenesulphon-m'-nitroanilide, formed small needles, m. p.  $207^{\circ}$  (Found: C, 47.4; H, 3.4.  $C_{19}H_{15}O_8N_3S_2$  requires C, 47.8; H, 3.1%).

Di-p-toluenesulphon-m'-nitroanilide, plates, m. p.  $180^{\circ}$  (Found: C, 54.1; H, 4.1.  $C_{20}H_{18}O_6N_2S_2$  requires C, 53.9; H, 4.0%).

m-Nitrobenzenesulphon-p'-nitro-o'-toluidide, prisms, m. p.  $189^{\circ}$  (Found: C, 46.0; H, 3.6.  $C_{13}H_{11}O_6N_3S$  requires C, 46.3; H, 3.3%).

Di-m-nitrobenzenesulphon-p'-nitro-o'-toluidide, m. p.  $201^{\circ}$  (Found: C, 43.2; H, 2.7.  $C_{19}H_{14}O_{10}N_4S_2$  requires C, 43.7; H, 2.7%).

Di-m-nitrobenzenesulphon-o'-nitro-p'-toluidide, prisms, m. p.  $215^{\circ}$  (Found: C, 43.8; H, 2.7%).

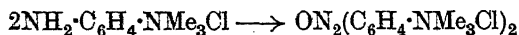
Di-m-nitrobenzenesulphon-o'-nitro-o'-toluidide, pale yellow needles, m. p.  $193^{\circ}$  (Found: C, 43.4; H, 2.6%).

Di-p-toluenesulphonanilide, large prismatic needles, m. p.  $183^{\circ}$  (Found: C, 59.7; H, 4.6.  $C_{20}H_{19}O_4NS_2$  requires C, 59.8; H, 4.7%).

CXXXV.—*Oxidation of p-Aminophenyltrimethylammonium Methosulphate and Some Quaternary Ammonium Derivatives.*

By AHMAD ZAKI.

It was proposed to compare the meta-directing power of the nitro- and the quaternary ammonium radical in one and the same nucleus by nitrating *p*-nitrophenyltrimethylammonium salts. It was, however, found impossible to synthesise the *p*-nitrophenyltrimethyl ammonium salt, a fact in itself not without significance. Methyl sulphate, very carefully purified, and *p*-nitrodimethylaniline interacted neither in benzene solution nor when heated under pressure. With methyl iodide, there was no reaction at 120° and carbonisation took place at 165°. *p*-Aminophenyltrimethylammonium chloride was then submitted to the oxidising action of Caro's salt, in the hope that the expected nitroso-derivative could be oxidised to the required nitro-compound. The product, however, proved to be the corresponding azoxy-compound:



When this was nitrated, a nitro-group entered each nucleus in the ortho-position with respect to the azoxy-group.

Although comparison between the nitro- and the quaternary ammonium group could not be undertaken in the direct manner proposed, yet the superiority of the latter group over the former in its characteristic effects is plainly indicated by the failure to obtain the quaternary nitroso-compound required as compared with the fact that *p*-nitroaniline when similarly oxidised gives about an 80% yield of *p*-nitrosonitrobenzene. The first stage in the oxidation of an aniline by Caro's salt gives the corresponding phenylhydroxylamine (Bamberger and Tschirner, *Ber.*, 1899, 32, 1675). A meta-directing group in the para-position would draw more or less heavily for electrons on the nuclear carbon atom carrying the hydroxylamino-radical, thereby increasing the conjugation of the tertiary nitrogen with the nucleus, at the same time decreasing its capacity for oxidation. The stronger the meta-directing group the less is the inclination of the hydroxylamino-nitrogen towards oxidation, and therefore the lower the state of oxidation of the final product. As an azoxy-compound represents a lower stage of oxidation than a nitroso-compound, the quaternary ammonium group must be more strongly meta-orienting than the nitro-group. A circumstance that gives strength to the ammonium radical in the present oxidation is that the reaction is carried out in aqueous solution and the salt is

therefore almost completely ionised. Oxidation could not be carried out in other solvents.

The same effect underlies the unreactivity of *p*-nitrodimethylaniline towards methyl sulphate and methyl iodide. If this is the true explanation, one would expect less resistance in the ortho-compound and still less in the meta-compound. Accordingly experiments were carried out on *o*- and *m*-nitrodimethylaniline as well as on dimethylaniline itself. The last compound reacted vigorously with methyl sulphate in the cold in benzene solution, with the *m*-compound boiling was necessary, and no reaction occurred with the *o*-compound. The resistance of the *o*-compound to this addition is, however, limited, as it reacts with methyl iodide on heating under pressure (Friedländer and Dinesmann, *Monatsh.*, 1898, 19, 636). The same order obtains for the solubility of these anilines in acids.

*p*-Dimethylaminobenzaldehyde, *p*-aldehydophenyltrimethylammonium methosulphate, and nitrosodimethylaniline condensed readily with diketohydrindene and with *p*-aminophenyltrimethylammonium chloride.

#### EXPERIMENTAL.

*Action of Methyl Sulphate on Nitrosodimethylaniline.*—The two substances reacted very slowly in benzene. In molecular proportion, without a solvent or in ethereal solution, they reacted vigorously. The dark red oily product was washed with ether and benzene and left in a vacuum over sulphuric acid for many weeks; it thickened considerably but failed to crystallise (Found: N, 9.9.  $C_{10}H_{16}O_5N_2S$  requires N, 10.2%). In aqueous solution it gave barium sulphate on treatment with barium chloride, but no precipitate with perchloric or picric acid. Boiling alkali liberated a volatile base having the odour of dimethylamine. The compound would therefore appear to be the  $\psi$ -methosulphate corresponding to the  $\psi$ -methiodide prepared by Knorr (*Ber.*, 1897, 30, 934).

*p*-Acetamidophenyltrimethylammonium Methosulphate.—To a boiling benzene solution of *p*-acetamidodimethylaniline (1 mol.) was added a benzene solution of methyl sulphate (1.5 mols.), with shaking. After 10 minutes' boiling, the mixture was cooled and the colourless crystals were collected, washed with benzene (yield, practically theoretical) and recrystallised from alcohol; the methosulphate then melted at 165° (Found: C, 47.2; H, 6.5.  $C_{12}H_{20}O_5N_2S$  requires C, 47.4; H, 6.6%).

*p*-Aminophenyltrimethylammonium Methosulphate.—The preceding compound (1 g.) was heated on the water-bath with 10 c.c. of concentrated hydrochloric acid for 2½ hours: titration with

standard sodium nitrite then showed that the hydrolysis was complete. Heating with concentrated sulphuric acid (2 c.c.) and water (3 c.c.) for 5 hours caused almost complete hydrolysis, but the use of smaller concentrations of the acid or heating for a shorter time resulted in incomplete hydrolysis.

*p*-Acetamidophenyltrimethylammonium methosulphate (3 g.) was hydrolysed with hydrochloric acid and then diazotised with sodium nitrite (0.68 g.) at 0°. The cold solution was neutralised with sodium carbonate and mixed with  $\alpha$ -naphthol (1.44 g.) dissolved in an equivalent of aqueous sodium carbonate. After a few hours, addition of perchloric acid to the crimson solution precipitated *p*- $\alpha$ -naphtholazophenyltrimethylammonium perchlorate, which crystallised from 90% alcohol in red needles, m. p. 247° (decomp.) (Found: N, 10.3.  $C_{19}H_{20}O_5N_3Cl$  requires N, 10.3%).

The perchlorate of the  $\beta$ -naphthol compound, similarly prepared, had m. p. 267° (decomp.) (Found: N, 10.1%).

A similarly diazotised solution was treated with  $\alpha$ -naphthylamine in dilute hydrochloric acid. *p*- $\alpha$ -Aminonaphthaleneazophenyltrimethylammonium chloride, which was slowly precipitated, crystallised from alcohol-dilute hydrochloric acid in long reddish-violet needles, m. p. 196° (decomp.) (Found: N, 14.5.  $C_{19}H_{21}N_4Cl.HCl$  requires N, 14.8%).

*p*-Dimethylaminobenzeneazophenyltrimethylammonium Perchlorate.—Molecular quantities of nitrosodimethylaniline and *p*-aminophenyltrimethylammonium chloride were boiled together in hydrochloric acid solution and perchloric acid was then added. The long brown needles of the perchlorate that had formed after 24 hours were recrystallised from dilute perchloric acid solution. They charred above 280° (Found: N, 11.4.  $C_{17}H_{23}O_4N_4Cl.HClO_4$  requires N, 11.6%).

*p*-Dimethylaminobenzylidene - *p*-aminophenyltrimethylammonium Perchlorate.—When *p*-dimethylaminobenzaldehyde (1 mol.) and *p*-aminophenyltrimethylammonium chloride (1 mol.), each in hydrochloric acid solution, were mixed, a greenish-yellow colour developed at once, indicating that the condensation in this case takes place at the ordinary temperature. The mixture was boiled to complete the reaction, concentrated, and perchloric acid added. The copious precipitate obtained crystallised from dilute perchloric acid solution in orange-red needles, m. p. 253° (decomp.) (Found: N, 8.6.  $C_{18}H_{24}O_4N_3Cl.HClO_4$  requires N, 8.7%).

*Oxidation of p*-Aminophenyltrimethylammonium Chloride.—The solution in hydrochloric acid obtained by hydrolysis of the acetyl compound (see p. 1079) was neutralised with aqueous sodium hydroxide, cooled with ice, and treated with the equivalent amount



of ammonium persulphate made into Caro's salt by Willstätter's method (*Ber.*, 1909, **42**, 1842). The deep brownish-red solution of azoxybenzene-*pp'*-bistrimethylammonium chloride produced was kept for several hours and the following three salts were then prepared from it.

(1) The *perchlorate*,  $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_3\cdot\text{ClO}_4)_2$ , precipitated by the addition of perchloric acid to the neutral or slightly alkaline solution, crystallised from a mixture of dilute aqueous perchloric acid and alcohol in needles which varied in colour from yellow to brown and red. It melted and decomposed at  $268^\circ$ , sometimes with violent explosion (this property made the estimation of carbon and hydrogen impossible) (Found: N, 10.7, 10.6, 10.8; Cl, 13.7.  $\text{C}_{18}\text{H}_{26}\text{O}_9\text{N}_4\text{Cl}_2$  requires N, 10.9; Cl, 13.8%), and was identical with the synthetic perchlorate described on p. 1084.

(2) The *picrate*, precipitated from the neutral solution of the salt with aqueous picric acid, crystallised from much acetone and water (10:8) after several hours in needles; m. p.  $244^\circ$  (decomp.). It was analysed after several crystallisations. Notwithstanding its explosiveness, determinations of carbon and hydrogen were successful twice, a large excess of copper oxide and a very long copper spiral being used (Found: C, 46.9, 46.7; H, 4.2, 4.2; N, 18.0.  $\text{C}_{30}\text{H}_{30}\text{O}_{15}\text{N}_{10}$  requires C, 46.7; H, 4.2; N, 18.2%).

(3) The ferricyanide was obtained by the addition of a solution of potassium ferricyanide. This salt is a very sparingly soluble, uncrystallisable, greenish-yellow substance. When it is boiled with a slight excess of copper sulphate solution, and the filtered liquid is freed from copper and sulphate ions by baryta, and then from barium by passage of carbon dioxide, the final filtrate contains the quaternary carbonate, from which other salts can be obtained by neutralising the solution with the requisite acid.

The chloride was obtained by boiling the picrate with a large excess of concentrated hydrochloric acid. After cooling, the picric acid was removed by filtration and by repeated extraction with ether, and the filtrate evaporated to dryness on the water-bath. The deep red, glassy residue, which was extremely deliquescent, was crystallised from much absolute alcohol and dried in a vacuum desiccator. The straw-coloured needles of the chloride quickly reddened in the air. The highest melting point observed was  $252^\circ$  (decomp., preceded by considerable shrinkage).

The iodide was precipitated when solutions of the chloride and of sodium iodide in alcohol were mixed and was recrystallised from much methyl alcohol and dried in a vacuum desiccator; the orange plates obtained melted at  $198^\circ$  (decomp.). In the air the iodide absorbed moisture and turned brown.

*Volumetric Analysis of Azoxybenzene-pp'-bistrimethylammonium Perchlorate.*—This application of Knecht and Hibbert's titanous chloride method ("New Reduction Methods in Volumetric Analysis," 1925) to the estimation of the azoxy-group is novel. Through a mixture of 0.0300 g. of the perchlorate, 100 c.c. of water, and 10 c.c. of concentrated hydrochloric acid, carbon dioxide was passed for 10 minutes. The solution was then warmed to 60–70° and titrated with standard titanous chloride until the yellow colour was destroyed. Towards the end of the titration, at least 3 minutes were allowed after the addition of every 0.5 c.c. of the chloride, as the reduction was then by no means instantaneous. The end-point was not very sharp (Titres found : 26.2, 26.4, 26.0, 27.2 c.c. Calc. : 25.8 c.c.). The presence of the perchlorate ion has no effect on the titanous chloride at the dilution used, as was proved by blank experiments on potassium chlorate solutions. The indirect method (excess of titanous chloride and back-titration) was useless.

*Nitration of Azoxybenzene-pp'-bistrimethylammonium Salts.*—Nitric acid alone had no nitrating action on the azoxy-chloride; when the solution was evaporated to dryness, the *nitrate* remained. This crystallised from anhydrous methyl alcohol in small, light orange, needle-like prisms, m. p. 220–222° (decomp.). It was hygroscopic, but was practically insoluble in absolute alcohol and acetone (Found : N, 18.8.  $C_{18}H_{26}O_7N_6$  requires N, 19.2%).

When the nitrate (1.5 g.) was added to concentrated nitric acid (10 c.c.; *d* 1.42), followed by concentrated sulphuric acid (15 c.c.), a vigorous action took place with evolution of oxides of nitrogen in the cold. The solution was boiled for 1.5 hours, the resulting clear yellow liquid diluted and neutralised with sodium carbonate, and perchloric acid added. The *dinitroazoxybenzene-pp'-bistrimethylammonium perchlorate* obtained crystallised from aqueous alcohol in deep brown crystals, m. p. 265° (decomp.) {Found : N, 13.9.  $ON_2[C_6H_3(NO_2) \cdot NMe_3 \cdot ClO_4]_2$  requires N, 14.0%}. The corresponding *chloride*, obtained from the picrate by treatment with concentrated hydrochloric acid as previously described, crystallised from dilute hydrochloric acid in thin, reddish-brown, rectangular plates which melted with decomposition (Found : N, 17.3.  $C_{18}H_{24}O_5N_6Cl_2$  requires N, 17.7%).

The diamine produced by complete reduction of the nitro-compound with zinc and hydrochloric acid was an *o*-diamine, for it gave a deep wine colour with ferric chloride and condensed instantly with phenanthraquinone on the addition of a drop of alkali, giving a dark green precipitate.

*Diketohydrindene Condensations.*—These were undertaken with the object of comparing the reactivities of the nitroso- and the

aldehydo-group and of studying the effect on the reactivity of a quaternary ammonium group in the para-position.

*With nitrosodimethylaniline.* Molecular quantities of diketohydrindene and nitrosodimethylaniline were boiled together in absolute alcohol for 3 minutes. At once, a deep blood-red colour developed and a crystalline compound separated; this, after being washed with absolute alcohol and dried, melted at  $210^{\circ}$  (decomp.) (Found: N, 9.8.  $C_{17}H_{14}O_2N_2$  requires N, 10.1%).

*With p-dimethylaminobenzaldehyde.* The condensation was carried out as in the last experiment and took place just as quickly. The product separated from alcohol in crystals with a blue lustre, m. p.  $99-100^{\circ}$  (compare Noelting and Blum, *Ber.*, 1901, 34, 2467).

*With p-aldehydophenyltrimethylammonium methosulphate.* Equimolecular quantities of the methosulphate (see below) and diketohydrindene were boiled in absolute alcohol. The colour changed from yellow to orange and the reaction was complete in less than 5 minutes. Water was then added and the solution was extracted with benzene to remove any excess of diketohydrindene and boiled. On standing, the product separated in deep orange needles, which were washed with a little alcohol and dried; m. p.  $243^{\circ}$  (decomp.) (Found: N, 3.5.  $C_{20}H_{21}O_6NS$  requires N, 3.5%).

*With the azoxy-quaternary salts.* These were recovered unaltered when a similar condensation was tried with them.

*p-Aldehydophenyltrimethylammonium Methosulphate.*—Pure dry methyl sulphate was mixed in slight excess with *p*-dimethylaminobenzaldehyde and warmed very gently to start the reaction, which proceeded rather violently. The voluminous frothy product, on cooling, changed to a small, dark red, glassy mass which became crystalline in a few hours. The methosulphate, recrystallised from hot methyl alcohol, formed long yellow needles, which were washed with ether dried over sodium. They were extremely soluble in water and melted at  $138-139^{\circ}$  (Found: N, 5.2; OMe, nil.  $C_{11}H_{17}O_5NS$  requires N, 5.1%).

The perchlorate was precipitated from a solution of the methosulphate as an oil which slowly solidified. It crystallised from dilute perchloric acid solution after some time in yellow plates, m. p.  $140-141^{\circ}$  after being washed with absolute alcohol and dried. It was appreciably soluble in water and puffed strongly when heated in a flame (Found: N, 5.4.  $C_{10}H_{14}O_5NCl$  requires N, 5.3%).

*Benzylideneaniline - pp'-bistrimethylammonium Perchlorate.*—*p*-Aminophenyltrimethylammonium chloride in hydrochloric acid solution was boiled with an equivalent quantity of *p*-aldehydophenyltrimethylammonium methosulphate and perchloric acid was then added; after 2 days, long, thin, slightly yellow needles

had formed. These when dry became deep red at 240° and charred at about 260°. Heated in a flame, the compound exploded (Found: N, 8.2.  $C_{19}H_{27}O_8N_3Cl_2$  requires N, 8.4%).

*Addition of Methyl Sulphate to pp'-Tetramethyldiaminoazoxybenzene.*—Methyl sulphate ( $1\frac{1}{2}$  mols.) was added to the base (1 mol.), and enough benzene to ensure its solution on boiling, which was continued under reflux for an hour. The benzene was then decanted, the product washed with ether, and the coffee-brown crystalline residue dissolved in water. Addition of perchloric acid precipitated a perchlorate which, after being crystallised from alcohol-dilute perchloric acid solution and dried, melted, alone or mixed with the azoxy-perchlorate described on p. 1081, at 268° (decomp.). The two picrates also were identical.

*m-Nitrophenyltrimethylammonium Methosulphate.*—A mixture of *m*-nitrodimethylaniline (28 g.; 1 mol.); methyl sulphate (30 g.; 1.5 mols.), and benzene (25 c.c.) was heated in a water-bath for 1 hour. The heavy oil produced solidified on cooling, and after decantation of the benzene and washing with ether the residue crystallised from slightly aqueous alcohol in thin needle-like plates, m. p. 220°, which were very soluble in water (Found: N, 9.5.  $C_{10}H_{16}O_6N_2S$  requires N, 9.6%).

The *picrate* crystallised from water in yellow prismatic plates, m. p. 150° (decomp.) (Found: N, 17.1.  $C_{15}H_{15}O_9N_5$  requires N, 17.1%), and the *perchlorate* from dilute perchloric acid solution in white feathery needles, m. p. 230–232° (decomp.) (Found: N, 9.9.  $C_9H_{13}O_6N_2Cl$  requires N, 10.0%).

The *iodide*, obtained by adding a concentrated solution of sodium iodide to a solution of the methosulphate, crystallised from water in large white needles, m. p. 202° (Found: N, 8.9.  $C_9H_{13}O_6N_2I$  requires N, 9.1%).

*Phenyltrimethylammonium Methosulphate.*—When a solution of dimethylaniline (30 g.; 1 mol.) in benzene (20 c.c.) was treated with methyl-sulphate (30 g.; 1 mol.), it soon got hot and the benzene boiled away even through a reflux condenser. The oily product quickly solidified and then crystallised from acetone in colourless needles. The *perchlorate*, precipitated with perchloric acid from a solution of the methosulphate, crystallised from dilute perchloric acid solution in colourless needles (Found: N, 5.8.  $C_9H_{14}O_4NCl$  requires N, 5.9%).

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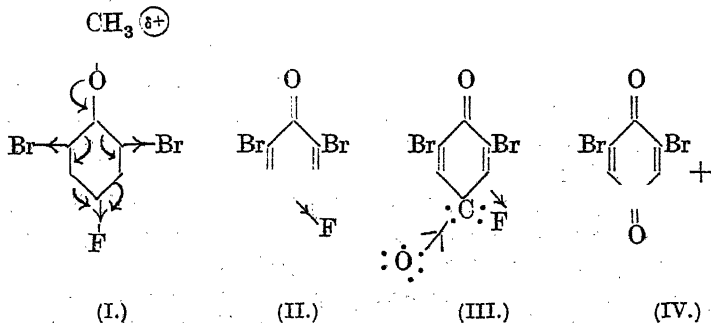
UNIVERSITY COLLEGE, LONDON. [Received, February 19th, 1930.]

CXXXVI.—*The Action of Fuming Nitric Acid on the 4-Halogeno-2 : 6-dibromo-phenols and -anisoles. Anomalous Behaviour of Fluorine Derivatives.*

By HERBERT HENRY HODGSON and JOSEPH NIXON.

KOHN and ROSENFELD (*Monatsh.*, 1925, **46**, 101) prepared 4-chloro-2 : 6-dibromo-3-nitro- and -3 : 5-dinitro-anisoles by the nitration of 4-chloro-2 : 6-dibromoanisole and of the mononitrated product. In an attempt to repeat their reaction with 4-fluoro-2 : 6-dibromoanisole, the product obtained was 2 : 6-dibromo-*p*-benzoquinone and consequently it appeared of interest to submit each of the 4-halogeno-2 : 6-dibromo-phenols and -anisoles to the action of fuming nitric acid in order to ascertain the rôle of the 4-halogen. All the phenols except the 4-iodo-compound (which was destroyed) gave 2 : 6-dibromo-*p*-benzoquinone, Kohn and Rosenfeld's results with 4-chloro-2 : 6-dibromoanisole (*loc. cit.*) were confirmed, and 2 : 4 : 6-tribromoanisole behaved similarly, *i.e.*, was mono- and di-nitrated. 4-Iodo-2 : 6-dibromoanisole, however, reacted anomalously to form 2 : 6-dibromo-4-nitroanisole.

The mechanism of reaction in the case of 4-fluoro-2 : 6-dibromoanisole can be regarded as a three-stage operation, *viz.*, the combined general effect (Allan, Oxford, Robinson, and Smith, J., 1926, 401) of the three halogens rendering the methyl group sufficiently mobile (positive) for detachment and oxidation (I); rearrangement of the residue to the quinonoid form (II), facilitated by the same general effect; and subsequent attack by oxygen (III) with separation of ionic fluorine (IV). The same mechanism will also apply to the phenols.



In the 4-chloro- and 4-bromo-2 : 6-dibromoanisoles, the combined general effect of the halogens is inadequate to produce the necessary reactivity (positivity) of the methyl group, and so normal nitration occurs. The above general effect is still further reduced in 4-iodo-

2 : 6-dibromoanisole, and consequently the methyl group remains intact, but the electron-donating power of the iodine is now sufficient to enable kationoid attack by the nitric acid to take place at the 4-carbon atom with nitration and elimination of iodine.

That fluorine exerts a far greater general effect than the other halogens is shown by the relatively much greater solubility of *p*-fluorophenol in water (indicating considerable ionisation) than is exhibited by the other *p*-halogenophenols, the order being  $F > Cl > Br > I$ , in accord with the order of general effects.

#### EXPERIMENTAL.

*Preparation of p-Fluorophenol.*—*p*-Fluoronitrobenzene, obtained in 25% yield by the authors' method for *m*-fluoronitrobenzene (J., 1928, 1879), was reduced by means of tin and hydrochloric acid to *p*-fluoroaniline, which was converted into *p*-fluorophenol by the standard procedure (Hodgson, E.P. 200,714).

4-Fluoro-2 : 6-dibromophenol was obtained when a solution of *p*-fluorophenol (11.2 g.) in water (250 c.c.) was treated gradually and shaken vigorously with a solution of bromine (10 c.c.; 2 mols.) in water (80 c.c.) containing potassium bromide (27 g.). The voluminous white precipitate produced was filtered off and washed with water; it crystallised from dilute alcohol in colourless needles, m. p. 48° (Found : Br, 59.2.  $C_6H_3OFBr_2$  requires Br, 59.3%).

4-Fluoro-2 : 6-dibromoanisole.—Methylation of the above phenol was best carried out by Haworth and Lapworth's procedure in xylene solution with methyl sulphate and potassium carbonate (J., 1923, 123, 2986), the direct method with methyl sulphate and caustic alkali giving poor yields. The product crystallised from light petroleum in small colourless needles, m. p. 55° (Found : Br, 56.5.  $C_7H_5OFBr_2$  requires Br, 56.3%).

*Action of Fuming Nitric Acid on the 4-Halogeno-2 : 6-dibromophenols and -anisoles.*—*General procedure.* The substance (5 g.) was dissolved in ice-cold nitric acid (50 c.c.;  $d$  1.5), the mixture poured after 15 minutes on ice, and the resulting precipitate crystallised from alcohol.

*Results.* (1) 4-Fluoro-2 : 6-dibromo-phenol and -anisole each gave 2 : 6-dibromo-*p*-benzoquinone, m. p. and mixed m. p. 130—131° (Found : Br, 59.9, 60.2. Calc. : Br, 60.1%).

(2) 4-Chloro-2 : 6-dibromophenol gave 2 : 6-dibromo-*p*-benzoquinone, whereas 4-chloro-2 : 6-dibromoanisole gave 4-chloro-2 : 6-dibromo-3-nitroanisole, m. p. 58°, and this on further nitration with a mixture of fuming nitric and concentrated sulphuric acids gave 4-chloro-2 : 6-dibromo-3 : 5-dinitroanisole, m. p. 146° (compare Kohn and Rosenfeld, *loc. cit.*)

(3) 2:4:6-Tribromophenol gave 2:6-dibromo-*p*-benzoquinone, and 2:4:6-tribromoanisole gave 2:4:6-tribromo-3-nitroanisole, which crystallised in small colourless plates, m. p. 82° (Found: N, 3.9; Br, 61.8.  $C_7H_4O_3NBr_3$  requires N, 3.6; Br, 61.5%), and gave 2:4:6-tribromo-3:5-dinitroanisole, which crystallised from alcohol in colourless needles, m. p. 148° (Found: N, 6.6; Br, 55.5.  $C_7H_3O_5N_2Br_3$  requires N, 6.4; Br, 55.2%), on further nitration as above.

(4) 4-Iodo-2:6-dibromophenol (m. p. 105°; prepared by direct dibromination of *p*-iodophenol in glacial acetic acid; compare King and McCombie, J., 1913, 103, 222) was completely destroyed by ice-cold fuming nitric acid.

2:6-Dibromo-4-iodoanisole, prepared from the above phenol by Haworth and Lapworth's method (*loc. cit.*), crystallised from light petroleum in colourless needles, m. p. 78° (0.1310 g. gave 0.2040 g. of mixed silver halides. Calc.: 0.2036 g.). On nitration with fuming nitric acid as above, 2:6-dibromo-4-nitroanisole was obtained, which crystallised in long colourless needles; the m. p. and mixed m. p. with an authentic specimen, prepared by dibromination of *p*-nitrophenol and subsequent methylation, was 122° (Found: N, 4.8; Br, 51.7. Calc.: N, 4.5; Br, 51.5%).

The authors desire to thank the British Dyestuffs Corporation for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD.

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## CXXXVII.—*Polycyclic Aromatic Hydrocarbons. Part I.*

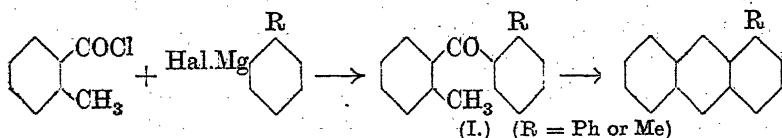
### 1- and 2-Phenylanthracenes and Derivatives of 1:2-Benzanthracene.

By JAMES WILFRED COOK.

THE substance responsible for the cancer-producing properties of tars and mineral oils is probably a polycyclic aromatic hydrocarbon of very high boiling point, and the hydrocarbons to be described in this and subsequent communications have been prepared in the course of a search for an active carcinogenic substance of known structure. The correlated experiments on animals are being conducted by E. L. Kennaway and the fluorescence spectra of the pure hydrocarbons have been examined by I. Hieger for comparison with the characteristic banded spectrum of tars and other cancer-producing mixtures (for example, the products of the action of

aluminium chloride upon 1:2:3:4-tetrahydronaphthalene). The results of Kennaway and Hieger are published elsewhere (*Biochem. J.*, in the press).

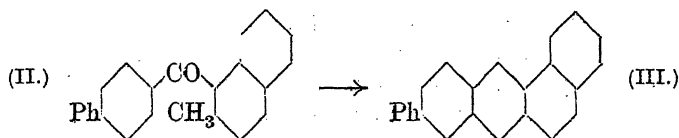
Of the three possible structural isomerides of monophenylanthracene only the *meso*-compound has hitherto been described. 1- and 2-Phenylanthracenes have now been prepared, the former by pyrolysis of 2-*o*-toluoyldiphenyl (I; R = Ph) obtained from magnesium 2-diphenyl iodide and *o*-toluoyl chloride, and the latter by reduction of 2-phenyl-9-anthrone :



1-Phenylanthracene resembles 1-methylanthracene in its ready solubility and fusibility, whereas 2-phenylanthracene, like the 2-methyl compound, is sparingly soluble and high-melting. When *di-o*-tolyl ketone (I; R = CH<sub>3</sub>), prepared from magnesium *o*-tolyl bromide and *o*-toluoyl chloride, was boiled for a long time, it underwent the condensation of an *o*-methyl benzophenone derivative to an anthracene derivative discovered by Elbs (*Ber.*, 1884, **17**, 2848; 1886, **19**, 408; *J. pr. Chem.*, 1886, **33**, 185; 1887, **35**, 471; 1890, **41**, 1) and recently extended by Morgan and Coulson (*J.*, 1929, 2203, 2551) and by Clar and his co-workers (*Ber.*, 1929, **62**, 351, 940, 951, 1574, 3021). The product was not 1-methylanthracene, however, but anthracene itself, one methyl group being eliminated from the ketone. This observation emphasises the need for confirmation of structures assigned to  $\alpha$ -alkylanthracenes obtained by pyrogenic means. For instance, H. Meyer and Bernhauer (*Monatsh.*, 1929, **53** and **54**, 731) obtained an anthracene hydrocarbon, m. p. 199°, by distillation of benzyl-*o*-xylene, but were in error in regarding their product as 1-methylanthracene, which has been shown by several investigators to melt at 86° (*e.g.*, von Braun and Bayer, *Ber.*, 1926, **59**, 916). The formation of 1:3-dimethylanthracene by pyrolysis of benzylmesitylene (Louise, *Ann. Chim.*, 1885, **6**, 185) shows that this loss of  $\alpha$ -methyl groups is not universal. 2-Methylanthracene and its derivatives have frequently been obtained by pyrogenic methods (*e.g.*, *Eng. Pats.* 251,270; 253,911; Elbs, *loc. cit.*; Morgan and Coulson, *loc. cit.*), but no case of loss of a  $\beta$ -methyl group appears to have been recorded.

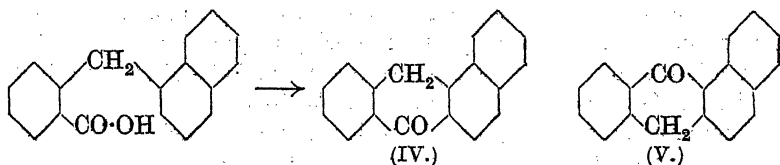
6-Phenyl-1:2-benzanthracene (III) was formed by pyrolysis of 1-*p*-phenylbenzoyl-2-methylnaphthalene (II), obtained from 2-methylnaphthalene and *p*-phenylbenzoyl chloride :





Reduction of 3-methyl-1:2-benzanthraquinone (Scholl and Tritsch, *Monatsh.*, 1911, **32**, 997) with zinc dust and potassium hydroxide, although slow and incomplete, led to 3-methyl-1:2-benzanthracene. 1:2-Benzanthraquinone reacted normally with magnesium phenyl bromide to give 9:10-diphenyl-9:10-dihydro-1:2-benzanthraquinol, which was reduced by zinc dust in boiling acetic acid to 9:10-diphenyl-1:2-benzanthracene. Subsequent to this preparation these two compounds were described by Clar (*Ber.*, 1930, **63**, 118).

1:2-Benz-10-anthrone (IV), formed by dehydration of 1-naphthylphenylmethane-2'-carboxylic acid, was converted by benzoic anhydride in pyridine solution into 1:2-benzanthranyl 10-benzoate, m. p. 171°, whereas reduction of 1:2-benzanthraquinone with aluminium powder and concentrated sulphuric acid led to an anthrone (V), which gave the isomeric 1:2-benzanthranyl 9-benzoate, m. p. 202—203°. These two benzoates were obtained by Barnett and Matthews (*Chem. News*, 1925, **130**, 339) from the mixture of anthrones obtained by reduction of benzanthaquinone with tin and hydrochloric acid and the methods of preparation now given require transposition of the orientations suggested by these authors.

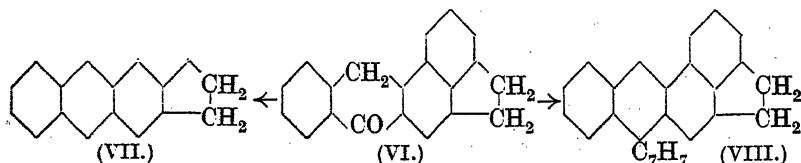


1:2-Benz-10-anthrone reacted normally with magnesium benzyl chloride. The resulting 10-hydroxy-10-benzyl-9:10-dihydro-1:2-benzanthracene was dehydrated to 10-benzyl-1:2-benzanthracene, and the same hydrocarbon was also formed in small yield when 1:2-benzanthracene was heated with benzyl chloride and zinc dust in carbon disulphide solution (compare Lippmann and Fritsch, *Monatsh.*, 1904, **25**, 793). Treatment of 1:2-benz-10-anthrone with magnesium methyl iodide yielded only resinous products, and the same remark applies to the action of magnesium benzyl chloride on 1:2-benz-9-anthrone.

With the object of obtaining intermediate compounds from which 9:10-dibenzyl-1:2-benzanthracene might be prepared by a method analogous to that previously used for dibenzyl-

anthracene (Barnett and Cook, J., 1928, 567), 1:2-benz-9-anthrone and 1:2-benz-10-anthrone were heated with benzyl chloride and potassium hydroxide solution. Both anthrones yielded only resinous products. When 1:2-benzanthraquinone was heated with benzyl chloride and alkali in presence of sodium hydrosulphite, similar resinous products were formed, together with a small amount of a substance which had the composition and properties of a *benzyloxybenzanthracene*. Such a compound might conceivably be formed by monobenylation and reduction of 1:2-benzanthraquinol. The anticipated benzyhydroxybenzanthrone was not isolated.

3-Acenaphthylphenylmethane-2'-carboxylic acid was completely sulphonated in 2 hours by concentrated sulphuric acid at room temperature, but was dehydrated by zinc chloride to acenaphthanthrone (VI), not obtained pure but characterised as the acetate of its enol. This anthrone was reduced by zinc dust and sodium hydroxide to *acenaphthanthracene* (VII) and was converted by magnesium benzyl chloride into an unstable dihydroanthranol which passed into *benzylacenaphthanthracene* (VIII):



An attempt to condense acenaphthylene with phthalic anhydride was unsuccessful, the acenaphthylene being polymerised by aluminium chloride to the polyacenaphthylene, m. p.  $345\text{--}350^\circ$ , described by Dziewoński and Leyko (*Ber.*, 1914, 47, 1685).

Experiments are in progress which have as their object the preparation of derivatives of chrysene and other condensed 4-ring hydrocarbons together with more highly condensed compounds. It is probable that 3:4-benzphenanthrene has not yet been prepared, since the compound so described by Weitzenböck and Lieb (*Monatsh.*, 1912, 33, 564) may equally well be 1:2-benzanthracene, which has more recently been shown to have the same m. p. as their hydrocarbon.

## EXPERIMENTAL.

### *Phenylanthracenes.*

*o*-Iododiphenyl.—This compound was mentioned by Bachmann and Clarke (*J. Amer. Chem. Soc.*, 1927, 49, 2049), who gave no description of its preparation. It was readily obtained in 70% yield by the addition of a concentrated aqueous solution of potassium

iodide to a diazotised solution of *o*-aminodiphenyl\* in dilute sulphuric acid. The crude *iodo*-compound was twice distilled in a vacuum and then formed a colourless viscous oil, b. p.  $140^{\circ}/3-4$  mm. (Found: C, 53.2; H, 3.5.  $C_{12}H_9I$  requires C, 51.4; H, 3.2%). The high figure obtained for carbon was probably due to the presence of diphenyl, but the substance was sufficiently pure for the subsequent experiments.

*2-o-Toluoyldiphenyl* (I; R = Ph).—A Grignard solution prepared from *o*-iododiphenyl (20 g.), magnesium turnings (1.7 g.), and ether (45 c.c.) was added slowly, with agitation, to *o*-toluoyl chloride (10 c.c.) diluted with ether (30 c.c.) and cooled to  $-10^{\circ}$ . After  $\frac{1}{2}$  hour at  $-10^{\circ}$ , the solution was allowed to warm slowly and then boiled for an hour. The product was decomposed with ice and hydrochloric acid, and the crude ketone freed from unchanged acid chloride by passing steam into its alkaline suspension for  $\frac{1}{2}$  hour. It was then dried in ethereal solution with sodium sulphate and distilled in a vacuum. The chief fraction was collected at  $190-192^{\circ}/3-4$  mm. The distillate, a yellowish syrup, was obtained in 55% yield as a colourless crystalline powder, m. p.  $66-67^{\circ}$ , by crystallisation from light petroleum (Found: C, 88.3; H, 5.95.  $C_{20}H_{16}O$  requires C, 88.2; H, 5.9%). This *ketone* gave a yellow solution in concentrated sulphuric acid.

*1-Phenylantracene*.—The aforesaid ketone (5 g.) was boiled gently for  $7\frac{1}{2}$  hours, and the product distilled. The red wax-like distillate was triturated with acetic acid and the solid in suspension was collected after 2 days and recrystallised from alcohol. The product (0.85 g.) was obtained pure by recrystallisation from ligroin and then twice from alcohol. It formed small, pale yellow prisms, m. p.  $110-112^{\circ}$ , readily soluble in the usual media (Found: C, 94.1; H, 5.6.  $C_{20}H_{14}$  requires C, 94.5; H, 5.5%).

*2-Phenylantracene*.—2-Phenyl-9-anthrone (5 g.) (Scholl and Neovius, *Ber.*, 1911, **44**, 1078) was reduced with zinc dust (15 g.) activated with copper, and 2*N*-sodium hydroxide solution (100 c.c.). The product, after extraction of the zinc with hydrochloric acid, was recrystallised from methyl ethyl ketone and then from ethyl acetate. 2-Phenylantracene formed small, pale yellow leaflets, m. p.  $207-207.5^{\circ}$ , sparingly soluble in most media (Found: C, 94.2; H, 5.4%).

#### *Di-o-tolyl Ketone.*

A Grignard solution prepared from *o*-bromotoluene (36.5 g.), magnesium turnings (5.1 g.), and ether (100 c.c.) was added slowly, with agitation, to *o*-toluoyl chloride (30 c.c.) diluted with ether (100

\* The author is indebted to Professor G. T. Morgan, F.R.S., for a gift of the *o*-aminodiphenyl used in this experiment.

c.c.) at  $-10^{\circ}$ . After  $\frac{1}{2}$  hour the solution was allowed to warm and then boiled for an hour. The product was decomposed with ice and hydrochloric acid, and the crude *ketone* freed from unchanged *o*-toluoyl chloride and distilled (b. p.  $307-308^{\circ}$ ). The solid distillate was recrystallised from methyl alcohol (yield, 25 g.) and then formed colourless needles, m. p.  $64-67^{\circ}$  (Found: C, 85.6; H, 6.5.  $C_{15}H_{14}O$  requires C, 85.7; H, 6.7%).

*Pyrolysis.* Di-*o*-tolyl ketone (5 g.) was boiled gently for 24 hours, and the product distilled. The distillate was diluted with alcohol and the resulting crystals were collected and recrystallised from ethyl acetate, forming colourless plates, shown by the method of mixed melting points to consist of pure anthracene. After removal of the solvents from the mother-liquor, oxidation of the residue with chromic acid in glacial acetic acid yielded anthraquinone but no anthraquinonecarboxylic acid.

#### *Derivatives of 1:2-Benzanthracene.*

6-*Phenyl-1:2-benzanthracene*.—(i) Anhydrous aluminium chloride (11.5 g.) was slowly added to 9.4 g. of *p*-phenylbenzoyl chloride\* (Scholl and Seer, *Annalen*, 1912, 394, 148; Wieland and others, *ibid.*, 1927, 452, 7) and 2-methylnaphthalene (6.5 g.) in carbon disulphide (50 c.c.). After 3 hours, the reaction was completed by  $\frac{1}{2}$  hours' heating on the water-bath. The product was decomposed with ice and hydrochloric acid, the carbon disulphide distilled off, and the steam-volatile by-products removed. The residue was dried and distilled in a vacuum (b. p.  $265^{\circ}/4-5$  mm.). The distillate, an amber-coloured resin, was dissolved in hot ligroin, and the solution cooled. The resulting crystalline solid was obtained analytically pure by two recrystallisations from methyl alcohol. 1-*p*-Phenylbenzoyl-2-methylnaphthalene (II) formed colourless needles, m. p.  $109-110^{\circ}$  (Found: C, 89.4; H, 5.6.  $C_{24}H_{18}O$  requires C, 89.4; H, 5.6%). The solution in sulphuric acid was cherry-red.

(ii) 1-*p*-Phenylbenzoyl-2-methylnaphthalene (4 g.) was boiled gently for  $\frac{1}{2}$  hour, and the dark-coloured residue distilled. The distillate was recrystallised from benzene (yield, 0.3 g.) and then from ethyl acetate. 6-*Phenyl-1:2-benzanthracene* (III) formed pale yellow leaflets, m. p.  $240-241^{\circ}$  (Found: C, 94.4; H, 5.3.  $C_{24}H_{16}$  requires C, 94.7; H, 5.3%). This compound gave a crimson solution with a yellowish-green fluorescence in concentrated sulphuric acid. On gentle warming, the colour became purple and then

\* *p*-Phenylbenzoic acid was obtained in good yield by oxidation of 4-acetyldiphenyl (Adam, *Ann. Chim.*, 1888, 15, 255) with boiling alkaline potassium permanganate.

intensely blue. This colour reaction is shown by 1:2-benzanthracene itself and also by all its hydrocarbon derivatives so far examined with the exception of the 9:10-diphenyl derivative.

**3-Methyl-1:2-benzanthracene.**—3-Methyl-1:2-benzanthraquinone (5 g.), mixed with zinc dust (15 g.), was heated on the water-bath with concentrated aqueous ammonia (50 c.c.) diluted with water (25 c.c.). After 3 hours, the initial blood-red colour had faded to pale yellow but was restored by the addition of 50% potassium hydroxide solution (25 c.c.). After boiling for 20 hours, the solution was treated with a further 5 g. of zinc dust and then boiled for 50 hours. Reduction was still incomplete, but the product was collected and zinc removed by hydrochloric acid and unchanged quinone by boiling alkaline sodium hydrosulphite solution. The residue was recrystallised from pyridine and alcohol, glacial acetic acid, and benzene-light petroleum. 3-Methyl-1:2-benzanthracene formed almost colourless plates, m. p. 153–154° (Found: C, 94.1; H, 5.8.  $C_{19}H_{14}$  requires C, 94.2; H, 5.8%).

**1:2-Benz-10-anthrone (IV).**—Twenty g. of 1-naphthylphenylmethane-2'-carboxylic acid (Scholl, Seer, and Zinke, *Monatsh.*, 1920, 41, 601) were intimately mixed with anhydrous zinc chloride (60 g.) and heated at 180° for 20 minutes. The molten mass was cooled and extracted with water and then with dilute sodium carbonate solution, the latter treatment removing a small amount of unchanged acid. Purification of the crude anthrone (16 g.) was not feasible on account of its instability. This method of preparation gave much better results than dehydration of the acid with concentrated sulphuric acid, which led to considerable oxidation and sulphonation.

**1:2-Benzanthranlyl 10-benzoate** was formed when the anthrone was treated with benzoic anhydride and pyridine at 100°. It melted at 171–172°, in agreement with the figure given by Barnett and Matthews (*loc. cit.*) for the compound which they suggested was the 9-benzoate.

**1:2-Benzanthranlyl 10-acetate** was obtained when the above anthrone (3 g.) was treated at 100° for an hour with acetic anhydride (5 c.c.) and pyridine (20 c.c.). It formed straw-coloured needles, from benzene and alcohol, which melted at 156° to a cloudy liquid, becoming clear at 163° (Found: C, 83.7; H, 4.85.  $C_{20}H_{14}O_2$  requires C, 83.9; H, 4.9%).

**10-Hydroxy-10-benzyl-9:10-dihydro-1:2-benzanthracene.**—To a Grignard solution prepared from benzyl chloride (6 c.c.) and magnesium powder (1.5 g.), cooled in a freezing mixture, was added finely powdered 1:2-benz-10-anthrone (IV; 5 g.). After 2 hours, the product was allowed to warm to room temperature, kept over-

night, and decomposed with ice and ammonium chloride. The washed ethereal solution was evaporated, and the residual oil mixed with 2 volumes of hot alcohol. The crystalline solid obtained by cooling was recrystallised from benzene–light petroleum (Found : C, 89.2; H, 5.9.  $C_{25}H_{20}O$  requires C, 89.3; H, 5.95%). This *dihydroanthranol* formed a colourless crystalline powder, m. p. 153–153.5°. Treatment of its solution in boiling alcohol with a few drops of hydrochloric acid resulted in separation of a thick meal of crystals of 10-*benzyl*-1 : 2-*benzanthracene*, yellowish leaflets (from benzene), m. p. 195–196°, intensely fluorescent in solution (Found : C, 94.1; H, 5.6.  $C_{25}H_{18}$  requires C, 94.3; H, 5.7%). The same compound was also obtained in small yield when 1 : 2-*benzanthracene* (6.4 g.), benzyl chloride (6.75 c.c.), and zinc dust (0.5 g.) were heated together in carbon disulphide (50 c.c.) for 16 hours. After removal of the solvent from the filtered solution a viscous oil remained. Its ethereal solution slowly deposited the 10-*benzyl*-1 : 2-*benzanthracene*.

1 : 2-*Benz-9-anthrone* (V).—This was obtained when aluminium powder (12.5 g.) was slowly added with occasional cooling to a solution of 1 : 2-*benzanthraquinone* (50 g.) in concentrated sulphuric acid (500 c.c.). After 3 hours, the orange-yellow solution was poured into ice and water, and the precipitate collected and dried in a vacuum desiccator. The resulting brown powder was recrystallised from chloroform, in which it was extremely easily soluble. It could not be obtained analytically pure on account of its instability, but was converted by benzoic anhydride in pyridine into the benzoate, m. p. 201–202°, described by Barnett and Matthews (*loc. cit.*). This benzoate, which depressed the m. p. of the 10-benzoate, is clearly 1 : 2-*benzanthranyl* 9-benzoate.

*Benzylation of Benzanthraquinol*.—A boiling suspension of 1 : 2-*benzanthraquinone* (5.2 g.) in 10% potassium hydroxide solution (100 c.c.) was treated with excess of sodium hydrosulphite and then with benzyl chloride (4.6 c.c.). After 2 hours' boiling, addition of more potassium hydroxide solution (20 c.c.) and benzyl chloride (1 c.c.) resulted in rapid fading of the red colour of the solution. Steam-volatile products were removed and the residual resin was dissolved in hot alcohol. The solution yielded, on cooling, a small amount of crystalline material, which was recrystallised from benzene and alcohol. The substance, probably 10-*benzyloxy*-1 : 2-*benzanthracene*, formed colourless needles, m. p. 178–179°. Its solutions in benzene and in sulphuric acid were fluorescent, and alcoholic alkali produced no "anthranol colour" (Found : C, 90.1; H, 5.6.  $C_{25}H_{18}O$  requires C, 89.8; H, 5.4%).

*Acenaphthanthrone* (VI).—3-Acenaphthylphenylmethane-2'-carboxylic acid (12 g.), prepared by reduction of the corresponding keto-

acid with zinc and sodium hydroxide (compare Lorriman, *J. Amer. Chem. Soc.*, 1925, 47, 215), was dehydrated with zinc chloride (36 g.) in the manner described for the preparation of 1 : 2-benz-10-anthrone. The acenaphthanthrone, obtained in good yield, had little power of crystallisation and was characterised as the *acenaphthanthranyl acetate*, obtained with acetic anhydride and pyridine at 100° and recrystallised from xylene. This acetate formed straw-coloured needles, m. p. 229–230° (Found : C, 84.5; H, 5.15.  $C_{22}H_{16}O_2$  requires C, 84.6; H, 5.1%).

*Acenaphthanthracene* (VII).—The aforesaid anthrone (from 12 g. of acid) was reduced by boiling for 16 hours with zinc dust (35 g.) and 2*N*-sodium hydroxide solution (200 c.c.). The product, after extraction of zinc with hydrochloric acid, was crystallised from acetic acid (yield, 4 g.) and obtained analytically pure by recrystallising it twice from xylene and twice from benzene. This *hydrocarbon* formed yellow plates, m. p. 192°, and gave the usual benzanthracene colour reaction with sulphuric acid (Found : C, 94.5; H, 5.5.  $C_{20}H_{14}$  requires C, 94.5; H, 5.5%).

10-*Benzylacenaphthanthracene* (VIII).—Acenaphthanthrone (VI; 1 mol.) was treated with magnesium benzyl chloride (3 mols.) as described in the case of 1 : 2-benz-10-anthrone. The intermediate dihydroanthranol was unstable and partly dehydrated to the hydrocarbon even by boiling alcohol. Conversion was completed by crystallisation from glacial acetic acid and the product was finally recrystallised twice from ethyl acetate. 10-*Benzylacenaphthanthracene* formed pale yellow needles, m. p. 199–200° (Found : C, 93.9; H, 5.8.  $C_{27}H_{20}$  requires C, 94.2; H, 5.8%).

The author desires to express his thanks to Mr. F. Goulden for valuable assistance in the preparation of material.

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[Received, March 14th, 1930.]

## CXXXVIII.—*The Dismutation of Some Disulphides.*

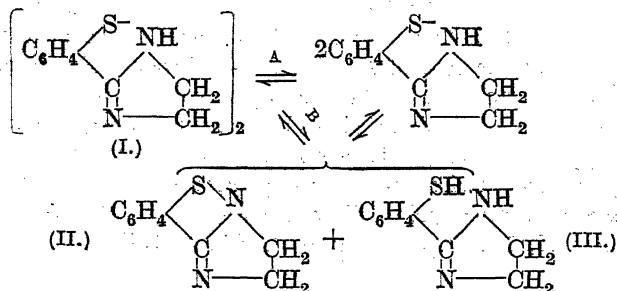
By ERNEST WILSON McCLELLAND and LEONARD ARTHUR WARREN.

FURTHER investigation of 2 : 2'-*oo'*-dithiodiphenyl-4 : 5-dihydroglyoxaline (I) (McClelland and Warren, *J.*, 1929, 2623) shows that this disulphide exhibits anomalous properties in solution. Molecular-weight determinations of the material in alcohol and benzene by the ebullioscopic method give low values which diminish with

dilution (Table I). The low values obtained cannot be ascribed to reaction of solvent and solute, since the latter when recovered is identical with the original and gives values in agreement with those obtained in the initial experiment. Moreover, the apparent molecular weight of the disulphide at a given concentration is constant even on prolonged boiling; it is thus evident that the anomalous results are not due to decomposition but accord with a reversible dissociation of the disulphide.

Solutions of the disulphide are thermochromic, the intensity of the colour increasing with rise of temperature and decreasing on cooling again. This property has previously been observed by Lecher (*Ber.*, 1915, 48, 524) in certain disulphides and has been attributed to a weakening of the S-S link. The dihydroglyoxaline disulphide, unlike the disulphides investigated by Lecher, shows a marked divergence from Beer's law (Table III).

These unusual properties of the disulphide might be accounted for by dissociation in solution to free radicals (A), or by a reversible change of the type (B) which may be termed reversible dismutation.



It is evident that process (A) may be regarded as the preliminary stage in the formation of the products (II) and (III) and thus any proof of dismutation (B) does not exclude the formation of free radicals as the initial stage of the dismutation. It is noteworthy that tetra-arylhydrazines (Wieland, *Annalen*, 1911, 381, 200; Wieland and Lecher, *ibid.*, 1912, 392, 156) and hexaphenylethanes (Schmidlin and García-Banús, *Ber.*, 1912, 45, 1344) undergo irreversible dismutation which appears to be dependent on the formation of free radicals from these substances.

Since solutions of the dihydroglyoxaline disulphide do not react with oxygen, and no evidence of abnormal reactivity could be obtained, the production of free radicals with anything more than a transitory existence appears to be excluded; indeed their formation although possible is not necessary to an explanation of the phenomena. Evidence proving the formation of the products of dis-



mutation (II and III) is forthcoming from the following independent sources.

The apparent molecular weight of the disulphide (I) in alcohol to which the free thiol (III) has been added is higher than that in the pure solvent and increases with increasing concentration of the thiol (Table II); this result accords with reversible dismutation of the disulphide to thiol (III) and the tricyclic compound (II). Moreover, the disulphide is formed by treatment of an equimolecular mixture of the tricyclic hydrobromide and the thiol with one equivalent of alkali; the yield of disulphide excludes the possibility of its formation by decomposition of the tricyclic compound and leads to the conclusion that the thiol and the free tricyclic compound react to give the disulphide in equilibrium with these; direct proof of this cannot be obtained, as the tricyclic compound itself has not been isolated.

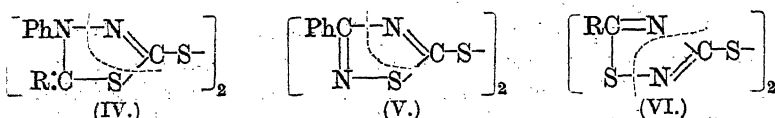
Further evidence of the dismutation process (B) is obtained from the action of methyl iodide on the disulphide, which gave the hydriodide of the *S*-methyl ether of the thiol (III) together with the hydriodide of the tricyclic compound (II); the formation of these products is readily accounted for by dismutation of the disulphide to thiol and tricyclic compound, the hydrogen iodide liberated in the methylation of the thiol forming salts of the *S*-methyl ether and of the tricyclic compound, thus permitting the isolation of the latter salt.

Substitution of the imino-hydrogen of the dihydroglyoxaline disulphide (I) should inhibit dismutation, since cyclisation would be prevented. Unfortunately, attempts to prepare the requisite derivatives have been unsuccessful.

The behaviour of 2:2'-mm'- and 2:2'-pp'-dithiodiphenyl-4:5-dihydroglyoxalines has been studied in comparison with that of the ortho-compound. These disulphides have now been synthesised from the amides of mm'- and pp'-dithiobenzoic acids. The nitriles, obtained from these, on treatment with ethylenediamine in presence of hydrogen sulphide were readily converted into the dihydroglyoxaline disulphides and thiols; the *S*-methyl ethers of the latter have also been prepared. Normal values for the molecular weight of these disulphides were obtained. Owing to the improbability that the tricyclic system could be formed from the *m*- and *p*-disulphides, it was not anticipated that they would show dismutation in solution, but it was considered that a variation in the stability of the S-S link might exist. The *p*-disulphide, like the *o*-compound, is readily reduced by hydrogen sulphide, but the *m*-compound is not reduced to the thiol. This variation in stability indicates that the dihydroglyoxaline nucleus tends to weaken the S-S link when

in the *o*- or *p*-position to it but not in the *m*-, and the effect is probably an electronic one. The instability of the S-N link when in the *o*-position to the  $\text{-C=N-}$  group (McClelland and Warren, *loc. cit.*, p. 2624) appears to be of a similar character.

The authors are not aware of any previously recorded example of reversible dismutation. Irreversible dismutation has been observed in the thiodiazoline series (Busch, *Ber.*, 1895, 28, 2635); *e.g.*, disulphides of the type (IV,  $\text{R} = \text{H}_2$ ) when kept in chloroform yield the corresponding thiols and the endocyclic compounds.

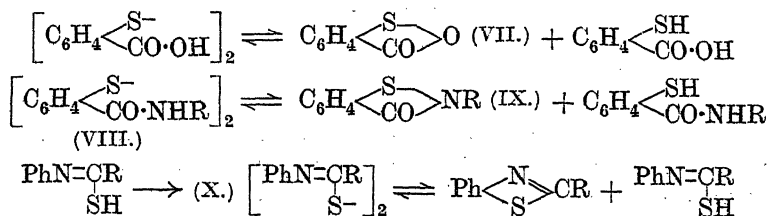


The presence of the  $\text{N}=\text{C}_n\text{-S}$  complex in these compounds ( $n = 1$ ) and in the *o*-dihydroglyoxaline disulphide (I,  $n = 3$ ) is significant and suggests that such a complex in a disulphide tends to weaken the S-S link; the reaction of the thioketothiodiazoline disulphides (IV,  $\text{R} = \text{S}$ ) with methyl iodide (Busch and Lingenbrink, *J. pr. Chem.*, 1900, 61, 330) or ammonia (Busch, *Ber.*, 1896, 29, 2127) to give *S*-methyl ethers or sulphamines confirms this view.

Further evidence is forthcoming from the relative ease of formation of mercaptides from disulphides, which may be taken as an indication of the stability of the S-S link. Many disulphides do not react with mercury (compare Konek, *Ber.*, 1920, 53, 1666) or do so only under intense conditions (Lecher, *ibid.*, p. 589). On the other hand, the thioketothiodiazoline disulphide (IV,  $\text{R} = \text{S}$ ) and disulphides of the types (V and VI,  $\text{R} = \text{Cl}, \text{OH}$ ) which contain the  $\text{N}=\text{C}_n\text{-S}$  complex readily give mercaptides with this metal (Söderbäck, *Annalen*, 1928, 465, 184). The formation of mercaptides from antipyrine and homoantipyrine disulphides (Konek, *loc. cit.*) suggests that the  $\text{O}=\text{C}_n\text{-S}$  complex may have a similar influence; the effect of such groups on the stability of disulphides is being investigated.

Reversible dismutation affords a convenient explanation of many reactions of disulphides. The condensation of 2:2'-dithiobenzoic acid with aromatic hydrocarbons (Prescott and Smiles, *J.*, 1911, 99, 640) to give thioxanthenes, in which the intermediate formation of a sulphenic acid has been postulated, may be regarded as the reaction of the dismutation product (VII) with the hydrocarbon and is thus analogous to the formation of anthraquinones from phthalic anhydride (Baeyer and Caro, *Ber.*, 1874, 7, 968), and the formation of 3-hydroxy-1-thionaphthen and its 2-derivatives

(Hutchinson and Smiles, J., 1912, **101**, 570) may be interpreted on the same basis.



The oxidation of substituted 2:2'-dithiobenzamides (VIII) (McClelland, Warren, and Jackson, J., 1929, 1584) to the *N*-substituted saccharins instead of to the disulphoxides may be ascribed to the dismutation of the amides into ketobenzisothiazoles (IX), which have previously been shown to be readily oxidised to the saccharins (McClelland and Gait, J., 1926, 921). The production of thiazoles by the oxidation of thioanilides and thiourethanes (Jacobson, *Ber.*, 1886, **19**, 1067) may be attributed to the dismutation of an intermediate disulphide (X, R = Ph, OEt) containing the N=(C)<sub>n</sub>-S complex.

#### EXPERIMENTAL.

The molecular weight of 2:2'-*oo'*-dithiodiphenyl-4:5-dihydroglyoxaline (I) (J., 1929, 2626) was determined by the Menzies-Wright method (*J. Amer. Chem. Soc.*, 1921, **43**, 2314). Values typical of those obtained are recorded below. Those given under (a) and (b) refer to different specimens, and under (c) the value obtained with material recovered after one of these experiments is given.

TABLE I.

Solvent: ethyl alcohol. <i>M</i> , calc., 354.									
	(a)		(b)						(c)
Conc. (g./l.) ...	3.19	7.05	0.669	1.58	2.40	3.67	5.15	6.47	4.095
Apparent <i>M</i> ...	232	264	168	177	227	236	247	251	243
Solvent: benzene.	Conc. (g./l.)		0.649		1.60				
	Apparent <i>M</i>		303		307				

*The Effect of the Presence of the Thiol (III) on the Apparent Molecular Weight of the Disulphide (I).*—The elevation of the boiling point of ethyl alcohol (31.8 c.c.) produced by the disulphide (0.1028 g.) was determined in the usual way; successive quantities of the thiol were added, and the resulting elevations noted. From these values the elevation due to the thiol alone, calculated from the experimental value 185.5, was deducted, whence the apparent

molecular weight of the disulphide in presence of the thiol was calculated.

TABLE II.

Apparent <i>M</i> of disulphide .....	243	304	336	360
Weight (g.) of thiol added .....	—	0.0694	0.1243	0.1800

*The Divergence from Beer's Law of Alcoholic Solutions of the Disulphide (I).*—Solutions of the disulphide of different concentrations were matched against a given length of a standard solution of the disulphide in a colorimeter. Three determinations (a, b, c) with different lengths of the standard column were made. Under (C) are given the lengths of columns of a solution of the disulphide of concentration *C* which matched the standard; under  $\frac{1}{2}C$  and  $\frac{1}{4}C$  are given the corresponding lengths for solutions of a half and a quarter of the concentration *C*. The theoretical values (Beer's law) are given in parentheses.

TABLE III.

	Lengths (cm.) of standard.	C.	$\frac{1}{2}C$ .	$\frac{1}{4}C$ .
(a)	2.0	3.2	4.8 (6.4)	5.8 (12.8)
(b)	4.0	5.9	8.5 (11.8)	13.2 (23.6)
(c)	6.0	9.8	13.9 (19.6)	16.1 (39.2)

*Methylation of the Disulphide (I).*—A solution of the disulphide (4 g.) in ethyl alcohol (200 c.c.) and methyl iodide (5 c.c.) was heated on the water-bath till almost colourless (about 10 minutes). Alcohol (100 c.c.) was distilled off; the hydriodide (1.7 g.) which crystallised on cooling was dissolved in hot water and treated with silver nitrate, and the precipitated iodide filtered off. Excess of potassium bromide was added to the filtrate; the hydrobromide which crystallised on cooling, after purification from alcohol, had m. p. 257°, alone or mixed with an authentic specimen of the hydrobromide of the tricyclic compound (II) (J., 1929, 2627). The alcoholic mother-liquor after removal of the hydriodide was diluted with water and concentrated; the material (3.2 g.) which crystallised was purified from water (charcoal). It had m. p. 206—208°, alone or mixed with the hydriodide of 2-*o*-methylthiolphenyl-4 : 5-dihydroglyoxaline (J., 1929, 2626), and on treatment with alkali gave a base, m. p. 98—100° alone or mixed with 2-*o*-methylthiolphenyl-4 : 5-dihydroglyoxaline (picrate, yellow needles, m. p. 207°).

*Reaction of 2-*o*-Thiolphenyl-4 : 5-dihydroglyoxaline (III) and the Tricyclic Compound (II).*—A mixture of the tricyclic hydrobromide (1 mol., from 0.45 g. of disulphide I) and the thiol (III) (1 mol.) in boiling alcohol was treated with aqueous potassium hydroxide (1 mol.), and the alcohol removed; the disulphide (I) (0.6 g.) was obtained from the residue.

**3 : 3'-Dithiobenzamide.**—3 : 3'-Dithiobenzoic acid (8 g.) (J., 1921, 119, 1792) was refluxed for  $\frac{1}{4}$  hour with an excess of thionyl chloride and a trace of ferric chloride. After removal of the thionyl chloride, the product was poured on ice and treated with aqueous ammonia ( $d$  0.880); the resulting solid was washed with hydrochloric acid and crystallised from acetic acid (charcoal), giving colourless plates (6.0 g.), m. p.  $243^{\circ}$  (Found : N, 9.3.  $C_{14}H_{12}O_2N_2S_2$  requires 9.2%).

**3 : 3'-Dithiobenzonitrile.**—3 : 3'-Dithiobenzamide (5 g.) was refluxed in xylene (300 c.c.) with phosphoric oxide (5 g.) for 4 hours; the solution was filtered and the xylene removed in steam. The residual material (3.5 g.), purified from alcohol, had m. p.  $102-103^{\circ}$  (Found : S, 23.6.  $C_{14}H_8N_2S_2$  requires S, 23.9%).

**2-m-Thiolphenyl-4 : 5-dihydroglyoxaline.**—A solution of 3 : 3'-dithiobenzonitrile (6 g.) and ethylenediamine (6 c.c.) in alcohol (100 c.c.) was saturated with hydrogen sulphide at  $-10^{\circ}$ . The mixture was heated under pressure for  $1\frac{1}{4}$  hours at  $90-100^{\circ}$ , and the alcohol distilled off. The residual oil was extracted with hydrochloric acid (2*N*) and the extract was treated with charcoal, filtered, and concentrated. The hydrochlorides which separated were treated with excess of sodium hydroxide, the undissolved material (disulphide) was filtered off, and the filtrate treated with carbon dioxide. The precipitated thiol was purified from water, giving yellow needles, m. p.  $225-228^{\circ}$  after previous softening (Found : S, 17.8; *M*, 190.  $C_9H_{10}N_2S$  requires S, 18.0%; *M*, 178). 2-m-Thiolphenyl-4 : 5-dihydroglyoxaline is sparingly soluble in alcohol and readily soluble in acids and alkalis; it gives a transient red colour with ferric chloride.

**2 : 2'-mm'-Dithiodiphenyl-4 : 5-dihydroglyoxaline**, obtained by oxidation of an alkaline solution of the thiol with potassium ferricyanide, crystallised from alcohol (90% aqueous) in pale yellow, hexagonal plates, m. p.  $193^{\circ}$  (Found : S, 17.9.  $C_{18}H_{18}N_4S_2$  requires S, 18.1%). A series of molecular-weight determinations in alcohol at different concentrations gave values from 359 to 370 ( $C_{18}H_{18}N_4S_2$  requires *M*, 354), no regular variation in molecular weight with diminishing concentration was observed, and in no case was the observed value less than 354.

**2-m-Methylthiolphenyl-4 : 5-dihydroglyoxaline.**—2-m-Thiolphenyl-4 : 5-dihydroglyoxaline (0.46 g.) and methyl iodide (3 c.c.) in alcohol (30 c.c.) were heated on the water-bath till colourless. The hydriodide which separated crystallised from aqueous alcohol (charcoal) in pale brown needles, m. p.  $262-264^{\circ}$  (decomp.) (Found : I, 39.7.  $C_{10}H_{12}N_2S.HI$  requires I, 39.7%). The base, obtained in the usual way, crystallised from water in fine colourless needles, m. p.  $94-96^{\circ}$ .

The following *p*-compounds were prepared in a similar way to the *m*-compounds :

4 : 4'-*Dithiobenzamide* from 4 : 4'-dithiobenzoic acid (J., 1922, 121, 2024), m. p. 278° (with previous softening) (Found : S, 21.0.  $C_{14}H_{12}O_2N_2S_2$  requires S, 21.1%).

4 : 4'-*Dithiobenzonitrile*, pale yellow needles, m. p. 172—173° (Found : S, 23.9.  $C_{14}H_8N_2S_2$  requires S, 23.9%).

2-*p*-*Thiolphenyl*-4 : 5-*dihydroglyoxaline*.—4 : 4'-Dithiobenzonitrile (3 g.) and ethylenediamine (4 c.c.) in alcohol (100 c.c.) were saturated with hydrogen sulphide at -15° and heated under pressure at 100° for 1½ hours. The product, treated as in the preparation of the *m*-compound, gave the disulphide (0.6 g.) and the required material (0.98 g.), which separated from water in pale yellow needles, m. p. 290° (decomp.) (Found : S, 18.1.  $C_9H_{10}N_2S$  requires S, 18.0%). The *thiol* gives a green colour with ferric chloride.

2 : 2'-*pp'*-*Dithiodiphenyl*-4 : 5-*dihydroglyoxaline*, obtained in the previous experiment and by oxidation of the *thiol* in alkaline solution by potassium ferricyanide, separated from alcohol in very small, colourless crystals, m. p. 213° (Found : S, 18.4.  $C_{18}H_{18}N_4S_2$  requires S, 18.1%). Molecular-weight determinations in alcohol at different concentrations gave values from 367 to 381 ( $C_{18}H_{18}N_4S_2$  requires *M*, 354), no regular variation in molecular weight with varying concentration was observed, and in no case was the observed value less than 354.

2-*p*-*Methylthiolphenyl*-4 : 5-*dihydroglyoxaline* hydriodide, m. p. 237°, gave the base, which separated from water in colourless plates, m. p. 155—156°.

*Action of Hydrogen Sulphide on the Dithiodiphenyl-4 : 5-dihydroglyoxalines*.—Hydrogen sulphide was bubbled through a solution of 2 : 2'-*pp'*-dithiodiphenyl-4 : 5-dihydroglyoxaline (0.5 g.) in warm alcohol (50 c.c.) for 2 hours. The precipitated material was extracted with sulphuric acid (2*N*), and the filtered extract made alkaline; after removal of some unchanged disulphide (0.06 g.) which was precipitated at this stage, the solution was saturated with carbon dioxide; 2-*p*-thiolphenyl-4 : 5-dihydroglyoxaline (0.27 g.) was then obtained, m. p. 290° alone or mixed with an authentic specimen.

2 : 2'-*oo'*-Dithiodiphenyl-4 : 5-dihydroglyoxaline on similar treatment yielded 2-*o*-thiolphenyl-4 : 5-dihydroglyoxaline (0.35 g.), m. p. 242° alone or mixed with an authentic specimen. 2-*m*-Thiolphenyl-4 : 5-dihydroglyoxaline was not obtained when the *m*-disulphide was treated in a similar way with hydrogen sulphide.

CXXXIX.—*The Production of Fog in the Neutralisation of Alkali with Hydrogen Halides. Part II. The Significance of the Presence of Ammonia.*

By RICHARD WALTER ALDIS and JAMES CHARLES PHILIP.

THE earlier communication (Askew, J., 1927, 966) described an experimental study of the acid fogs obtained by passing a stream of air charged with hydrogen chloride or bromide through a solution of sodium hydroxide or other non-volatile alkali. Among the points investigated were the concentration of acid in the fog droplets, the dimensions of the latter, and the relation of the amount of fog formed to the concentration of the alkali solution. Further information on various aspects of the phenomenon was required, however, before the mode of production and the stability of the fogs could be adequately interpreted.

In the fresh work which was undertaken attention was first directed to the reproducibility of the results. Various minor modifications of the earlier apparatus and procedure failed to secure the desired degree of reproducibility, and it was only a fortunate circumstance which led to the discovery of the source of the difficulty. In two parallel series of experiments, designed to correlate the amount of fog produced with the concentration of the caustic soda solution, it was found that the quantities of fog obtained in the one series were throughout about twice as great as in the other. This serious discrepancy led to the recognition that the caustic soda solutions employed in the two series had been made up with distilled water from separate sources, and examination of the two waters showed that they differed appreciably in their content of ammonia, as proved by Nessler tests. This clue was followed up, and definite evidence was obtained that the production of fog under the given conditions was determined by the presence of traces of ammonia in the caustic soda solution. The quantitative results which support this view are set out below, but it may be stated that when ammonia is rigorously excluded or removed from the caustic soda solution the amount of fog produced is negligible.

EXPERIMENTAL.

*Apparatus and Procedure.*—The apparatus was in general the same as already described (Askew, *loc. cit.*), and it is necessary to refer only to a few modifications which have been introduced. It was thought desirable to improve the temperature control, and accordingly the vessel containing concentrated hydrochloric acid, in which the air current was saturated with hydrogen chloride, was

kept in a bath at 25°, and the dried mixture of gases was then passed through the fog production chamber, containing the alkali solution. This vessel, as well as the fog absorption tube, was immersed in the same thermostat as the hydrogen chloride saturator. Provision was made for renewing the acid in the saturator after each experiment.

The U-tube employed for collecting the fog was charged with asbestos wool and calcium chloride, so that the figures given below for "weight of fog" (in mg.) generally include the water vapour which accompanied the fog droplets. In some cases, where the composition of the fog itself was to be ascertained, the collecting tube was charged with asbestos wool only.

In the majority of the experiments the air-hydrogen chloride mixture was passed at a rate of about 200 c.c. per minute for 8—10 minutes, and this may be regarded as a standard run. The conditions were, of course, maintained constant in any one series of comparable experiments.

*Measurements and Observations.*—Following the discovery of the significance of traces of ammonia for the production of acid fogs under the conditions described above, the further investigation of the character and stability of the fogs was made with alkali solutions to which known quantities of ammonium chloride had been added initially. A series of experiments with increasing concentration of caustic soda, but the same initial concentration of ammonia in each case, showed that the amount of fog obtained in a standard run first increased, reached a maximum, and subsequently decreased. The results obtained in three such series are set out in Table I and represented graphically in Fig. 1.

TABLE I.

(a) $\text{NH}_3 = 0.00005\%$ .		(b) $\text{NH}_3 = 0.0005\%$ .		(c) $\text{NH}_3 = 0.002\%$ .	
Normality of NaOH.	Weight of fog (mg.).	Normality of NaOH.	Weight of fog (mg.).	Normality of NaOH.	Weight of fog (mg.).
0.1	10	0.1	102	0.1	158
0.5	50	0.4	170	0.48	250
1.2	65	0.85	192	0.55	264
2.4	50	2.0	155	0.88	250
4.8	5	3.5	78	2.0	198
				3.5	105

The figures in Table I indicate that the amount of fog increases as the ammonia concentration rises, but series of experiments carried out at constant caustic soda concentrations and with a much wider range of ammonia values show that the amount of fog tends to become steady. The results obtained in one such series, in which the sodium hydroxide was 0.84*N*, were as follows:

$\text{NH}_3$ , % .....	0.0001	0.00025	0.001	0.003	0.005	0.007
Weight of fog (mg.)	125	160	224	260	267	270



As already indicated, a number of experiments were made in which the fog, after being collected and weighed, was analysed for hydrochloric acid (by titration) and for ammonia (by Nessler tests). The strongly acid character of the fogs is proved by the figures in

FIG. 1.

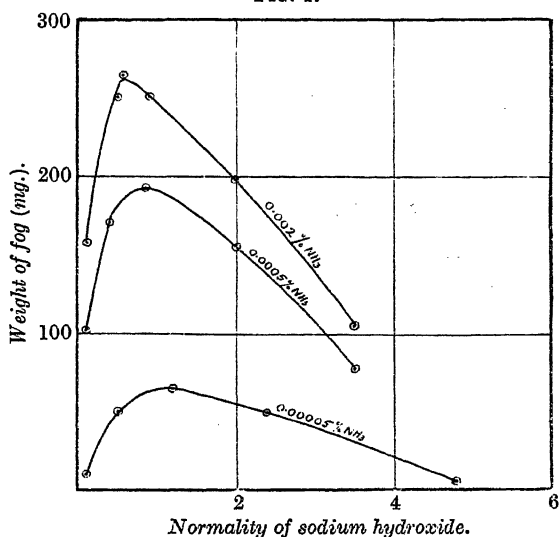


Table II, which show also that during each experiment a fair proportion of the ammonia was transferred from the caustic soda solution to the fog droplets.

TABLE II.

Normality of NaOH.	NH <sub>3</sub> initially, g.	Weight of fog (mg.).	Found in the fog.	
			NH <sub>3</sub> , g.	HCl, %.
0.39	0.00002	25	0.00001	5.9
0.39	0.00005	40	0.00002	5.9
0.39	0.0001	72	0.00005	5.8
0.39	0.0005	173	0.0003	5.8
0.39	0.001	246	0.0007	5.8
1.00	0.001	244	0.0005	6.4
3.90	0.001	106	0.0006	8.9

In some cases the passage of the acid-laden air stream was continued until fog formation practically ceased, and this was found to occur when the ammonia originally in the caustic soda had been transferred to the fog. Thus, for example, in one experiment the stream was bubbled through 100 c.c. of a 2.0*N*-caustic soda solution containing 0.002 g. of ammonia. When fog formation had practically ceased, after the passage of 12 litres of the gas mixture, the caustic soda solution was run out and found to be

1.75*N*, and to be free from ammonia. The fog formed during this experiment had been collected in a tube containing asbestos wool (previously shown to be free from ammonia). The wool was washed and the washings were made up to 200 c.c., aliquot portions being then tested with Nessler's solution. The total ammonia found in this way was equal to that originally present in the caustic soda solution.

In the earlier investigation it was observed that the amount of fog produced was markedly increased when small quantities of certain substances, such as gelatin and methylene-blue, were added to the alkali solution. These observations have been confirmed, and proof has been obtained that the substances in question owe their influence to the small quantities of ammonia liberated from them in caustic soda solution. It is noteworthy also that the ability to promote fog formation when an air-hydrogen chloride stream is passed through caustic soda is possessed, not only by ammonia, but by other volatile bases, such as methylamine and diethylamine.

The size of the droplets forming the fogs was estimated in the usual way by observing the rate of settling of the cloud. The value so obtained for the radius of the droplets varied somewhat according to the conditions under which the fog was produced, but was of the same order, *viz.*,  $10^{-4}$ — $10^{-5}$  cm., as that already recorded by Askew (*loc. cit.*). Definite evidence was obtained that the size of the droplets diminishes with increasing concentration of the caustic soda from which the fog was obtained.

Variation in the size of the droplets and the density of the fog, according to the vapour pressure of the surrounding medium, was further demonstrated by experiments in which thin fogs were passed through water. Thus, for example, a faint fog was obtained by bubbling the usual acid-air mixture through a concentrated (6*N*) caustic soda solution containing 0.002% of ammonia. This fog when bubbled through water became quite dense, but showed no change when bubbled through very concentrated solutions of potassium iodide or calcium chloride.

Further, when a fairly dense fog from the caustic soda solution was bubbled through concentrated sulphuric acid, it disappeared, but the inference that the fog had been absorbed was proved to be erroneous by subsequently passing the air stream through water, whereupon the fog reappeared, although in somewhat diminished intensity. The fact that concentrated sulphuric acid may render a fog invisible without absorbing it has been observed for ozone fogs (Rothmund, *Monatsh.*, 1918, **39**, 571), and for moist sulphur trioxide fogs (Remy, *Z. Elektrochem.*, 1922, **28**, 467).

Experiments carried out with the object of detecting any definite electrical charge on the fog droplets gave negative results. This is

in harmony with Askew's observations (*loc. cit.*, p. 978), as also with earlier investigations on the electrical condition of other chemical fogs (de Broglie and Brizard, *Compt. rend.*, 1909, **149**, 923; Rothmund, *loc. cit.*; Remy and Koch, *Z. anorg. Chem.*, 1924, **139**, 69).

#### Discussion.

The novel feature of the fogs described in this and the earlier communication is that they are strongly acid, although produced in an alkaline medium. Remy and his collaborators (*Z. angew. Chem.*, 1926, **39**, 147; *Z. anorg. Chem.*, 1927, **159**, 241), it is true, have shown that moist sulphur trioxide fogs can be bubbled through caustic potash solutions with only partial absorption, but these fogs were already formed before they came in contact with the alkaline medium.

Another important characteristic of the acid fogs described in the present paper is that their formation is conditional on the presence of ammonia (or other volatile alkali) in amounts which are very small compared with the quantity of acid contained in the droplets. The measurements and observations recorded above establish beyond doubt the significance of ammonia for the whole phenomenon, and warrant the view that the formation of ammonium chloride particles within the gas bubbles is the first and necessary stage in the production of the fog.

Such ammonium chloride particles, under the conditions prevailing, act as condensation nuclei, and droplets of solution are formed. These droplets then dissolve some of the hydrogen chloride in the gas bubble, and their vapour pressure is correspondingly lowered. This involves an increase in size by further condensation of water, the extent to which this takes place being determined mainly by the vapour pressure of the caustic soda solution surrounding the gas bubble.

Another consideration which is of significance in determining the stability of fogs such as those described above is the fact that the vapour pressure of a minute droplet of a liquid is greater than that at a plane surface. The bearing of this—as expressed by the Kelvin equation—on the stability of chemical fogs has been discussed by a number of earlier workers (Townsend, *Proc. Camb. Phil. Soc.*, 1899, **10**, 52; Rothmund, *loc. cit.*; Remy, *Chem. Zeit.*, 1928, **52**, 677). The vapour pressures for water droplets of radius  $10^{-4}$  and  $10^{-5}$  cm. are respectively about 0.1% and 1% greater than at a plane water surface at the same temperature. Hence, in an atmosphere saturated with water vapour in the ordinary way, such droplets would tend to disappear. They will be stabilised, however, even in such an atmosphere, if a compensating reduction of vapour pressure is effected by the presence of dissolved substances in the

droplets. Townsend (*loc. cit.*) has calculated that droplets of  $5 \times 10^{-5}$  cm. radius containing approximately 0.004 g. of sulphuric acid per g. of water would be stable in an atmosphere saturated with water vapour. It is assumed in the calculation that the sulphuric acid is completely ionised.

The fog droplets with which the present communication is concerned contain a much larger proportion of dissolved substance. Where the total amount of fog collected is small, the estimation of the acid which it contains is probably subject to a considerable error, but some of the figures recorded in Table II provide a basis for calculating the concentration of dissolved substance. The data of the experiment, for example, in which fog, weighing 246 mg., was produced from 0.39*N*-sodium hydroxide indicate that the droplets were approximately 1.5*N* as regards hydrochloric acid and 0.15*N* as regards ammonium chloride. Again, the solution constituting the droplets of the last experiment of Table II was approximately 2.5*N* as regards hydrochloric acid and 0.35*N* as regards ammonium chloride.

The fog droplets, of course, consist mainly of water, and the extent to which their concentration is altered by condensation or evaporation should be determined by the vapour pressure of water in the surrounding air. The measurements made so far and recorded above are not such as to permit the quantitative study of this adjustment, but attention is directed to one or two observations which are significant in this connexion. Thus, consideration of the last three experiments in Table II shows that, with increasing caustic soda concentration, the amount of acid in the droplets increases relatively to the water, and this means a lowering of the vapour pressure of the droplets. Again, an investigation of the size of the droplets obtained from caustic soda solutions of different concentrations showed a regular falling off with increasing alkali concentration.

It appears, however, that owing to the operation of certain factors, there are limits to the growth or shrinkage of droplets constituting a stable fog. If much water condenses on a droplet of radius  $10^{-4}$ – $10^{-5}$  cm., which is the stable range, it becomes so large as to settle very rapidly. If, on the other hand, a droplet within the stable range loses much water, the enhanced vapour pressure associated with high curvature may become the determining factor, with the result that the droplet becomes unstable and dries up. It is clear that further measurements are necessary in order to elucidate the relation between the vapour pressure of the droplets and that of the surrounding air.

The fact that the droplets, once formed inside the gas bubble, do not find their way to the surface of the bubble and get absorbed,

is probably due to their comparatively low mobility. The significance of this characteristic for the stability of chemical fogs has been discussed at length by A. Smith ("Text-book of Inorganic Chemistry," 1927, p. 482) and by Remy (*loc. cit.*, 1926 and 1927).

The character of the curves in Fig. 1 invites comment. The occurrence of a maximum is no doubt due to opposition between factors tending to increase the amount of fog and those which tend to diminish it. The vapour pressure of the ammonia in the caustic soda solution increases with increasing concentration of the latter, and this would lead to a larger number of nuclei and a greater weight of fog for a given run. Again, as the concentration of the caustic soda increases, it becomes more viscous, the air-acid mixture will form larger bubbles, and hence there is a greater chance of the droplets escaping in the air stream. The main factor operating in the reverse direction is the steady fall of water vapour pressure as the concentration of the caustic soda increases.

The observations recorded in this paper present one or two points of interest for the analytical chemist. The production of fog when an air-acid stream is passed through a solution of caustic soda is a sensitive test for small quantities of ammonia (or other volatile alkali) in the soda solution: the delicacy of the test approaches that of Nessler's solution. Further, it appears that the removal of hydrogen chloride from an air stream by passage through caustic soda solution is incomplete if the latter contains even small quantities of ammonia. In many of the experiments recorded above, as much as 10–15% of the hydrogen chloride escaped absorption in the caustic soda solution.

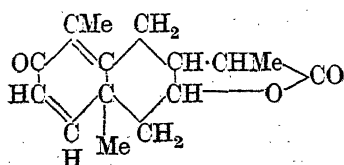
Under the conditions of the present work, where the factor of supersaturation is absent, the significance of hygroscopic nuclei for the production of fogs has been clearly demonstrated. In this connexion, it is interesting to note the view, now widely held by meteorologists, that atmospheric condensation does not normally commence on ordinary dust particles or on ions, but on hygroscopic substances. In view of the results of the present investigation, it seems possible that the small quantities of ammonia in the air may play a more important part in the production of atmospheric fogs than has been generally supposed.

One of the authors (R. W. A.) desires to express his thanks to the Department of Scientific and Industrial Research for a maintenance grant during the progress of the work described in the present communication.

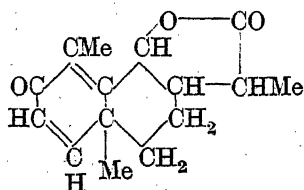
CXL.—*The Constitution of Santonin. Part II.*  
*The Synthesis of Racemic desmotropoSantonin.*

By GEORGE ROGER CLEMO, ROBERT DOWNS HAWORTH, and ERIC WALTON.

IN Part I (J., 1929, 2368) a constitution (I) was suggested for santonin and the  $\beta$ -position of the propionic acid side-chain was established by a synthesis of *dl*-santonous acid, and as a result, two formulæ (III and IV) can be suggested for the lactone desmotropo-santonin, which is prepared by the action of mineral acids on santonin (Andreocci, *Gazzetta*, 1893, **23**, ii, 469; *Ber.*, 1898, **31**, 3131). Structure (III) appears to have been generally accepted,

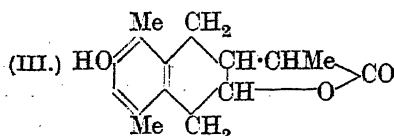


(I.)

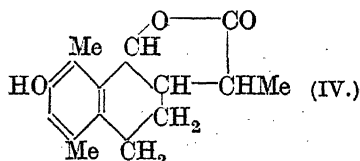


(II.)

although hitherto there has been no evidence to enable a decision to be made between the two formulæ and older publications (compare Gucci and Grassi-Cristaldi, *Gazzetta*, 1892, **22**, i, 1) employ structure (IV).



(III.)

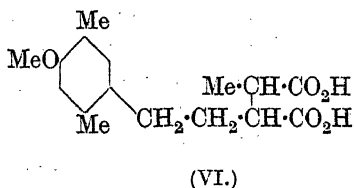
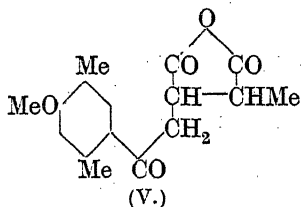


(IV.)

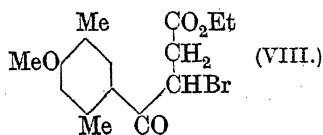
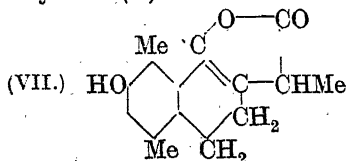
The present communication describes the synthesis of a lactone possessing the structure (IV), which is identical in all respects with racemic *desmotropo*santonin (Andreocci, *loc. cit.*). This synthesis establishes the  $\alpha$ -position of the lactonic oxygen atom and provides a further illustration of the preference shown in biosynthesis for the angular fusion of ring systems. At the same time, this necessitates a corresponding modification of the structure (I) which has been suggested for santonin and the structure (II), now adopted, is in agreement with the chemical behaviour of this substance.

The starting point in these synthetical experiments was ethyl  $\delta$ -4-methoxy-2:5-dimethylbenzoylbutane- $\beta\beta\gamma$ -tricarboxylate (XVI; R = Me in Part I), and an improved method is described for its conversion into  $\alpha$ -( $\beta$ -4-methoxy-2:5-dimethylphenylethyl)- $\alpha'$ -

methylsuccinic acid (VI). The tricarboxylate was hydrolysed with aqueous-alcoholic sodium hydroxide and the mixed racemates



of 8-4-methoxy-2:5-dimethylbenzoylbutane- $\beta\gamma$ -dicarboxylic acid (XVII; R = Me in Part I, compare p. 2385) were converted into the anhydride (V) by heating at 180°. One form only of this anhydride has been isolated, and when this was reduced by Clemmensen's method, the succinic acid derivative (VI) was obtained. Two racemic modifications of this acid were described in Part I (p. 2386), but the lower-melting isomeric only is obtained by reducing the anhydride (V).



The succinic acid derivative (VI) was refluxed with hydriodic acid and converted into  $\alpha$ -( $\beta$ -4-hydroxy-2:5-dimethylphenylethyl)- $\alpha'$ -methylsuccinic acid, which was not isolated in the crystalline state, but converted into the lactone (VII) of the enolic form of  $\alpha$ -7-hydroxy-1-keto-5:8-dimethyl-1:2:3:4-tetrahydronaphthyl-2-propionic acid by the action of warm concentrated sulphuric acid.

This lactone (VII) was not reduced by palladium and hydrogen in acetic acid solution, but with sodium amalgam in alcoholic solution, the lactone (IV) of  $\alpha$ -1:7-dihydroxy-5:8-dimethyl-1:2:3:4-tetrahydronaphthyl-2-propionic acid was obtained. This was identical with a specimen of racemic *desmotroposantonin*, prepared from santonin by the method outlined by Andreocci (*loc. cit.*), supplementary details of which will be found in the experimental section of this communication, and further the identity of the natural and the synthetic product has been confirmed by a comparison of their *acetyl* derivatives.

In Part I (p. 2374), the structure of ethyl 8-4-methoxy-2:5-dimethylbenzoylbutane- $\beta\gamma$ -tricarboxylate was discussed and an interesting result has now been obtained in an attempt to confirm the suggested structure. *Ethyl*  $\beta$ -bromo- $\beta$ -4-methoxy-2:5-dimethyl-

*benzoylpropionate* (VIII), prepared by bromination of *ethyl β-4-methoxy-2 : 5-dimethylbenzoylpropionate* (compare Part I, p. 2382), was condensed with ethyl sodiomethylmalonate. A tricarboxylate was obtained which, after hydrolysis and heating, gave the anhydride (V). This indicates that hydrogen bromide is eliminated in one or both of the methods for preparing the anhydride (V), and that the ethyl sodiomethylmalonate condenses with the acrylic ester derivative by a Michael reaction. These observations, however, do not demand any alteration in our views with regard to the structure of ethyl *δ-4-methoxy-2 : 5-dimethylbenzoylbutane-βγ-tricarboxylate*.

#### EXPERIMENTAL.

*Methyl and Ethyl β-4-Methoxy-2 : 5-dimethylbenzoylpropionates*.—*β-4-Methoxy-2 : 5-dimethylbenzoylpropionic acid* (5 g.) in methyl alcohol (30 c.c.) was saturated with dry hydrogen chloride with cooling in an ice-bath. After some hours, the mixture was refluxed for 2 hours on the water-bath, the bulk of the alcohol then removed, water added, followed by a slight excess of sodium hydroxide, the solid collected and dried (4.8 g.). Crystallisation from light petroleum (b. p. 80—100°) gave large colourless prisms (4.4 g.), m. p. 94—95° (Found: C, 67.1; H, 7.2.  $C_{14}H_{18}O_4$  requires C, 67.2; H, 7.2%). The *ethyl ester*, prepared similarly, formed stout colourless prisms, m. p. 49—50° (Found: C, 68.3; H, 7.3.  $C_{15}H_{20}O_4$  requires C, 68.2; H, 7.5%).

*Methyl and Ethyl β-Bromo-β-4-methoxy-2 : 5-dimethylbenzoylpropionates* (VIII).—A solution of bromine (3.5 g.) in light petroleum (b. p. 60—80°; 33 c.c.) was added to a solution of methyl *β-4-methoxy-2 : 5-dimethylbenzoylpropionate* (5 g.) in light petroleum (b. p. 60—80°; 40 c.c.); the bromine was rapidly decolorised and hydrogen bromide was evolved. The solvent was removed under reduced pressure; the residual oil crystallised from light petroleum (b. p. 40—60°) in large colourless prisms, m. p. 96° (Found: C, 51.3; H, 5.3; Br, 24.4.  $C_{14}H_{17}O_4Br$  requires C, 51.1; H, 5.1; Br, 24.3%). The *ethyl ester*, prepared similarly, separated from light petroleum (b. p. 40—60°) in large colourless prisms, m. p. 98—100°, which gave a considerable depression in m. p. when mixed with ethyl *α-bromo-β-4-methoxy-2 : 5-dimethylbenzoylpropionate* (compare Part I, p. 2382) (Found: C, 52.6; H, 5.6; Br, 23.1.  $C_{15}H_{19}O_4Br$  requires C, 52.5; H, 5.5; Br, 23.3%).

The ethyl ester was condensed with ethyl sodiomethylmalonate in benzene solution and the product after hydrolysis and heating yielded the anhydride, m. p. 171°, described below.

*δ-4-Methoxy-2 : 5-dimethylbenzoylbutane-βγ-dicarboxylic Anhydride* (V).—Ethyl *δ-4-methoxy-2 : 5-dimethylbenzoylbutane-βγ-tricarboxylate*.



oxylate (12 g.) was dissolved in ethyl alcohol (24 c.c.), sodium hydroxide (24 c.c. of 2*N*) added, and the mixture refluxed for 2 hours on the water-bath and then evaporated to a small bulk under reduced pressure. Water (30 c.c.) was added, and after standing, the precipitated 4-methoxy-2 : 5-dimethylacetophenone (0.5 g.) was filtered off. The filtrate was acidified with a mixture of concentrated hydrochloric acid (30 c.c.) and water (30 c.c.), the resulting milky emulsion rapidly extracted with ether, and the extract allowed partly to evaporate spontaneously over-night. The colourless 8.4-methoxy-2 : 5-dimethylbenzoylbutane- $\beta\gamma$ -dicarboxylic acid (5.3 g.) was collected and washed with a little ether and the ethereal filtrates were combined (A). The residue was heated in two portions for 1 hour in a metal-bath at 180°. After a brisk effervescence, a viscid, pale yellow gum resulted, which was stirred with ether while still warm and the colourless solid collected (2.85 g.). The ethereal filtrate on evaporation and reheating in the metal-bath gave 0.1 g. more of ether-insoluble solid. This solid was moderately easily soluble in boiling benzene, and separated in stout rhombic prisms, m. p. 171° (Found : C, 66.4; H, 6.2.  $C_{16}H_{18}O_5$  requires C, 66.2; H, 6.2%). The *anhydride* is insoluble in cold sodium hydroxide solution, and sparingly soluble in ethyl alcohol, from which it separates in jagged prisms. On evaporation of filtrate (A), a yellow viscid oily acid resulted, from which no solid could be obtained by solution in sodium hydroxide and reprecipitation with acid; but on being heated in a metal-bath as above, it gave 1.65 g. of the crude anhydride, together with a further 0.1 g. when the ethereal extract was again heated.

*Methyl 8.4-methoxy-2 : 5-dimethylbenzoylbutane- $\beta\gamma$ -dicarboxylate* was obtained on esterifying the anhydride with methyl alcohol and hydrogen chloride, and after distillation crystallised from light petroleum (b. p. 40—60°) in colourless prisms, m. p. 73—74° (Found : C, 64.3; H, 7.1.  $C_{18}H_{24}O_6$  requires C, 64.3; H, 7.1%).

$\alpha$ -( $\beta$ -4-Methoxy-2 : 5-dimethylphenylethyl)- $\alpha'$ -methylsuccinic Acid (m. p. 131—132°; compare Part I, p. 2386).—The anhydride (V) (1 g.), amalgamated zinc (5 g.), and concentrated hydrochloric acid (7 c.c.) were refluxed for 24 hours. The oil produced was decanted from the zinc residues, which were extracted with a small amount of ethyl alcohol, diluted with water and left over-night, and the colourless solid was collected and dried on porous plate (0.95 g.). The compound dissolved completely in hot benzene (4—5 c.c.) and on dilution with light petroleum (12 c.c.) gave colourless prisms, m. p. 131—132° (Found : C, 65.2; H, 7.8. Calc. : C, 65.3; H, 7.5%).

*Lactone of  $\alpha$ -7-Hydroxy-1-keto-5 : 8-dimethyl-1 : 2 : 3 : 4-tetrahydronaphthyl-2-propionic Acid (VII).*— $\alpha$ -( $\beta$ -4-Methoxy-2 : 5-dimethylphenylethyl)- $\alpha'$ -methylsuccinic acid (2.5 g.) was refluxed for 1 hour

with hydriodic acid (7.5 c.c.;  $d$  1.7), water (7.5 c.c.) added, the mixture extracted with ether, the extract freed from iodine by shaking three times with saturated sodium bisulphite solution and dried over sodium sulphate, and the ether removed.  $\alpha$ -( $\beta$ -4-Hydroxy-2:5-dimethylphenylethyl)- $\alpha'$ -methylsuccinic acid remained as a gum, which was stirred for 2 minutes in the water-bath with concentrated sulphuric acid (7.5 c.c.), the resulting dark brown solution cooled, and ice added; a straw-coloured gum was then obtained. After 1 hour, the dilute acid solution was decanted, the residue stirred with a cold saturated solution of sodium bicarbonate, and the colourless solid collected, washed with water, and dried on the water-bath. The material from three such experiments was dissolved in boiling acetic acid (80 c.c.) and water (10 c.c.), charcoal added to remove a faint purple coloration, and the filtrate diluted with boiling water (35 c.c.). On cooling, colourless, stout, rhombic prisms (3.1 g.), m. p. 250—253° (decomp.), separated (Found: C, 73.8; H, 6.8.  $C_{15}H_{16}O_3$  requires C, 73.8; H, 6.5%). The lactone is hydrolysed by warming for 15 minutes with methyl-alcoholic potassium hydroxide to give  $\alpha$ -7-hydroxy-1-keto-5:8-dimethyl-1:2:3:4-tetrahydronaphthyl-2-propionic acid, which dissolves in two-thirds strength acetic acid to give a persistent intense green solution, but crystallises from methyl alcohol in colourless prisms, m. p. 191° (Found: C, 68.4; H, 6.8.  $C_{15}H_{18}O_4$  requires C, 68.7; H, 6.9%).

*Synthetic Racemic desmotropoSantonin* (IV).—The above lactone (1 g.) was dissolved in ethyl alcohol (50 c.c.), washed sodium amalgam (80 g. of 4%) added, and the mixture refluxed for 15 hours on the water-bath. The solution was decanted from the mercury and filtered from a trace of sediment and the alcohol was removed under reduced pressure. The residue was dissolved in a small volume of water, acidified with hydrochloric acid, and extracted three times with ether and the extract was dried with sodium sulphate and evaporated to about 2 c.c. After 12 hours, 0.2 g. of a crystalline solid separated, m. p. 178—184°, raised to 194—196° after four recrystallisations from alcohol. When the above dried ethereal extract was evaporated, however, and the residue again refluxed over-night with alcohol (10 c.c.) and washed amalgam (40 g. of 4%), then, after removal of the alcohol and solution in water, acidification yielded a solid which was collected and crystallised once from alcohol, giving colourless prisms (0.3 g.), m. p. 199°, raised to 200—201° by one recrystallisation (Found: C, 73.4; H, 7.4.  $C_{15}H_{18}O_3$  requires C, 73.2; H, 7.3%). The compound is sparingly soluble in ethyl alcohol, readily in ethyl acetate, and almost insoluble in ether, and its m. p. is not depressed by admixture with racemic

*desmotroposantonin* prepared from *santonin* as described below. Synthetic *acetyl desmotroposantonin*, obtained by treatment with acetic anhydride and sodium acetate, separated in colourless prisms, m. p.  $146^{\circ}$ , again not depressed by mixture with *acetyl desmotroposantonin* prepared from *santonin* (Found: C, 71.1; H, 7.2.  $C_{17}H_{20}O_4$  requires C, 70.8; H, 7.0%).

*Racemic desmotropoSantonin from Santonin.*—*d-desmotropoSantonin* was prepared as follows: *Santonin* (10 g.) and fuming hydrochloric acid (60 c.c.) were heated in a sealed tube at  $35^{\circ}$  for 36 hours. The product was diluted with water, and the solid collected, dissolved in dilute sodium hydroxide solution, and filtered. The filtrate was acidified and warmed and the *d-desmotroposantonin* (8.5 g.) was collected; it crystallised from ethyl alcohol in fine prisms, m. p.  $260^{\circ}$  (compare Andreocci, *Gazzetta*, 1893, **23**, ii, 469). *isodesmotropoSantonin* was prepared from the *d*-form according to the method of Andreocci (*loc. cit.*), the reaction being complete in about  $1\frac{1}{2}$  hours. *isodesmotropoSantonin* melts at  $194^{\circ}$  [Andreocci gives  $187-188^{\circ}$  (decomp.)] and its acetyl derivative melts at  $154^{\circ}$ . *l-desmotropoSantonin* (the enantiomorph of *isodesmotroposantonin*) and racemic *desmotroposantonin* were prepared as described by Andreocci (*Ber.*, 1898, **31**, 3131).

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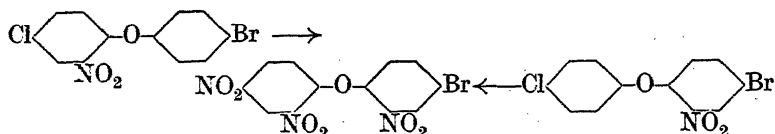
## CXLI.—The Scission of Diaryl Ethers and Related Compounds by Means of Piperidine. Part IV. Elimination of Halogen Atoms and Scission Reactions during Substitution Processes.

By DOROTHY LILIAN FOX and EUSTACE EBENEZER TURNER.

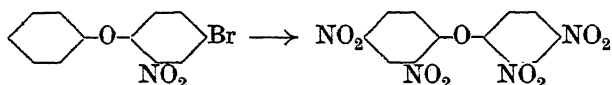
IN earlier investigations in the present series, a number of halogenated diphenyl ethers have been nitrated, with results that can be explained by current theories of aromatic substitution. We have now encountered some cases in which nitration is not of the simple type hitherto met with, but is accompanied by elimination of halogen atoms or disruption of the molecule.

The 2:2'-nitration of 4:4'-dichloro- and 4:4'-dibromodiphenyl ether proceeds without difficulty (J., 1927, 1168), and the mononitro-derivatives obtained by controlling the conditions of

nitration are readily convertible into the dinitro-compounds. We have now found that under the conditions which favour the formation of these dinitro-derivatives, both the 2- and the 2'-nitro-derivative of 4-chloro-4'-bromodiphenyl ether undergo partial elimination of chlorine, and that when the nitration is performed at 100°, complete elimination of chlorine occurs, with the formation of 4-bromo-2 : 2' : 4' -trinitrodiphenyl ether :



The same product is formed when the more drastic nitration conditions are applied to 4-chloro-4'-bromo-2 : 2' -dinitrodiphenyl ether. The latter compound may be obtained by nitrating either of the corresponding mononitro-compounds under definite conditions. Prolonged nitration of the bromotrinitro-ether causes very slow removal of the bromine atom. On the other hand, when 4-bromo-2-nitrodiphenyl ether is nitrated, the bromine atom is eliminated more readily, and with prolonged nitration pure 2 : 4 : 2' : 4' -tetranitrodiphenyl ether is produced :

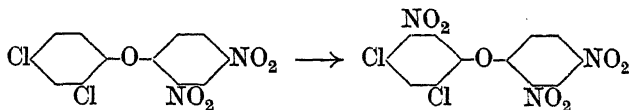


Elimination of chlorine occurs during the prolonged nitration of 4 : 4' -dichloro-2 : 2' -dinitrodiphenyl ether, but, in view of the above facts, it is surprisingly slow, and we have not succeeded in obtaining a pure specimen of the tetranitro-ether by this process. In short, the product of one replacement of chlorine by a nitro-group, namely, 4-chloro-2 : 2' : 4' -trinitrodiphenyl ether (compare the stability of the analogous bromo-compound) is relatively resistant. It is produced by the nitration of 4-chloro-2'-nitrodiphenyl ether, and, together with 4 : 4' -dichloro-2 : 2' -dinitrodiphenyl ether, by the hot nitration of 4 : 4' -dichloro-2-nitrodiphenyl ether.

There would appear to be three main factors determining such replacements of halogen by a nitro-group: (a) The factor that determines the course of ordinary aromatic substitution. In the present examples halogen and not hydrogen is eliminated. (b) The tendency of a co-valently attached halogen atom to become an ion. (c) The tendency of a halogen atom to remain in co-valent attachment to a carbon atom.

An excellent survey of the literature of atom or group elimination during substitution processes is given by de Lange (*Rec. trav. chim.*,

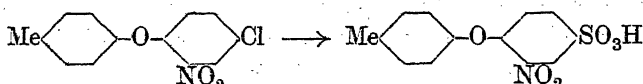
1926, 45, 19), and it is only necessary for present purposes to refer to a few general conclusions. It has usually been found that bromine is more readily eliminated than chlorine during nitration. Thus, for example, Ling (J., 1889, 55, 589) found that 2-chloro-4-bromo-6-nitrophenol was nitrated to give 2-chloro-4 : 6-dinitrophenol, and that 4-chloro-2-bromo-6-nitrophenol lost bromine in the *o*-position rather than chlorine in the *p*-, to give 4-chloro-2 : 6-dinitrophenol. That factor (*a*) is of greater importance than the nature of the halogen atom (factors *b* and *c*) would appear to be shown by the results of Hewitt and Mitchell (J., 1906, 89, 1167), who found that when diazotised *p*-nitroaniline was added to an alkaline solution of 1-chloro-, 1-bromo-, or 1-iodo- $\beta$ -naphthol, the product in each case was 1-benzeneazo- $\beta$ -naphthol. Again, it has already been shown (Parts II and III) that 2 : 4-dichloro- and 2 : 4-dibromo-2' : 4'-dinitrodiphenyl ethers readily undergo 5-nitration :



This occurs in the cold, but we have now submitted the two resulting trinitro-ethers to the action of fuming nitric acid at 100°. Although in both cases slight elimination of halogen occurs, almost the whole of the original substances may be recovered in the pure condition. It therefore seems probable that factor (*a*) is most important in these cases. In 4-chloro-4'-bromo-2- and -2'-nitrodiphenyl ether, the para-orienting effect of oxygen is the most powerful influence at work, whereas in 2 : 4-dichloro- and 2 : 4-dibromo-2' : 4'-dinitrodiphenyl ether this effect is more than counter-balanced by the 5-directing influence of the two halogen atoms, so that elimination of halogen does not occur. Again factor (*a*) takes control. The preferential elimination of chlorine from the chloro-bromo-ethers may be attributed to factor (*b*).

To some extent elimination reactions of the type under consideration are governed by mere mass effects in addition. For instance, bromination of 4-chloro-2 : 6-dinitrophenol under certain conditions causes replacement of a nitro-group by bromine, 4-chloro-2-bromo-6-nitrophenol being produced (Gordon, *Chem. News*, 1891, 63, 222), whilst picric acid, when gently warmed with bromine and water, gives 2-bromo-4 : 6-dinitrophenol (Armstrong, *Ber.*, 1873, 6, 650), and it is a common experience that in the chlorination of nitro-compounds at moderately high temperatures, nitrous fumes are occasionally given off, no doubt because partial elimination of the nitro-group has taken place.

A second type of elimination reaction has been observed in which a chlorine atom is replaced by the sulphonic acid group. Thus, when 4-chloro-2-nitro-4'-methyldiphenyl ether is dissolved in cold concentrated sulphuric acid, hydrogen chloride is at once evolved, and 2-nitro-4'-methyldiphenyl ether 4-sulphonic acid is formed :



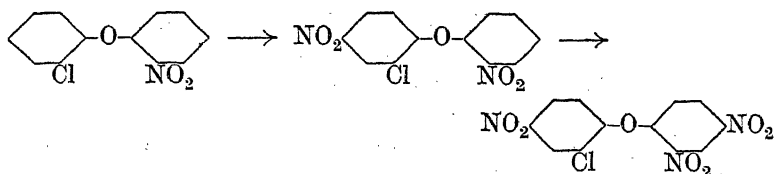
This result is unexpected, for no halogen hydride is produced by the action of cold concentrated sulphuric acid on the isomeric 4-chloro-2'-nitro-4'-methyldiphenyl ether, or on 2:4:4'-trichloro-, 2:4-dichloro-2':4'-dinitro-, or 2:4-dibromo-2':4'-dinitro-diphenyl ether.

A third type of reaction which has to be recorded is that of scission during nitration. By mild nitration, 4-chloro-2-nitro-4'-methyldiphenyl ether may be converted into 4-chloro-2:2'-dinitro-4'-methyldiphenyl ether, but, when it is dissolved in cold fuming nitric acid, the main product is 4-chloro-2:6-dinitrophenol. This phenol is also the main product formed by similarly nitrating 4-chloro-2'-nitro-4'-methyldiphenyl ether. Yet, although it is difficult to avoid concluding that in both nitrations the initial product is 4-chloro-2:2'-dinitro-4'-methyldiphenyl ether, the latter substance does not undergo scission when heated with fuming nitric acid, but suffers partial replacement of chlorine by a nitro-group.

The apparent destruction of a tolyl group during the above nitrations is interesting in view of the fact (Pauly, Gilmour, and Will, *Annalen*, 1914, 403, 119) that 3-nitro-*p*-cresol is converted by fuming sulphuric acid into  $\beta$ -methyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid. Incidentally, Reilly, Drumm, and Barrett (J., 1927, 67) have found that di-*p*-tolyl ether also undergoes considerable scission when nitrated.

A fourth set of results concerns the scission of certain ethers by piperidine. Although 4-chloro-2'-nitro-4'-methyldiphenyl ether readily undergoes scission by piperidine, 4-chloro-2-nitro-4'-methyldiphenyl ether is somewhat resistant to this reagent. Since, in general, 2- or 4-nitrodiphenyl ethers permit of facile piperidine scission, it would appear that the chlorine atom in 4-chloro-2-nitro-4'-methyldiphenyl ether acts in opposition to the nitro-group. A similar effect may be produced by a bromine atom; *e.g.*, *o*-bromonitrobenzene readily reacts with potassium phenoxide to give 2-nitrodiphenyl ether; but 2:5-dibromonitrobenzene reacts very indifferently.

The nitration of 2-chloro-2'-nitrodiphenyl ether has been found to proceed according to the following scheme :



The constitution of the chlorodinitro-ether follows from the fact that the ether is not identical with 2-chloro-2':4'-dinitrodiphenyl ether. 2-Bromo-2'-nitrodiphenyl ether is nitrated similarly.

Bromination of 4-bromo-2-nitrodiphenyl ether takes place in the 4'-position, for the product is identical with that obtained by the mononitration of 4:4'-dibromodiphenyl ether.

#### EXPERIMENTAL.

*Preparation of Diphenyl Ethers.*—The general procedure was as follows: Potassium hydroxide (1 mol.) was treated with so much water that a clear melt was obtained on heating to about 250° (about 1/10 to 1/15 mol.). The melt was then allowed to cool until incipient crystallisation began, and at once the phenolic substance (1 mol.) was rapidly added, with shaking. Subsequent procedure depended on the nature of the halogenonitro-compound to be used: (a) Halogenomononitro-compounds such as *o*-chloronitrobenzene, 2:5-dibromonitrobenzene, etc. In such cases, the halogenonitro-compound (1 mol.) was added in one portion to the still hot phenoxide melt, the whole was well shaken, and then heated under a short air-condenser in a metal bath at 160–180° for 3–4 hours. (b) Halogenodinitro-compounds, such as 1-chloro-2:4-dinitrobenzene. The halogenodinitro-compound (1 mol.) was added gradually with vigorous shaking during about 5 minutes. As a rule, potassium halide began to separate almost immediately, and the reaction was rendered complete by an hour's heating at 100°. In all cases, the reaction product was shaken with hot dilute alkali, and the cooled mixture filtered or extracted with ether, according to the nature of the final product.

It has not been found advisable to use copper-bronze as a catalyst in any of the condensations.

4-Chloro-4'-bromo-2'-nitrodiphenyl ether, prepared from *p*-chlorophenol and 2:5-dibromonitrobenzene, was crystallised from glacial acetic acid; it then melted at 100–101°. Raiford and Colbert (*J. Amer. Chem. Soc.*, 1926, **48**, 2652) gave m. p. 100.5°.

4-Chloro-4'-bromo-2-nitrodiphenyl ether, from *p*-bromophenol and 2:5-dichloronitrobenzene, had m. p. 95°. Raiford and Colbert (*loc. cit.*) gave m. p. 93–94°.

*4-Chloro-4'-bromo-2:2'-dinitrodiphenyl Ether.*—4-Chloro-4'-bromo-2'-nitrodiphenyl ether (3 g.) was added to a cold mixture of 15 g. of nitric acid ( $d$  1.5) and glacial acetic acid (15 g.). The solution was gently warmed until the solid had dissolved, and then poured into water. The precipitated solid crystallised from glacial acetic acid in very pale yellow, silky needles, m. p.  $165^{\circ}$  (0.1482 g. gave 0.1350 g.  $\text{AgCl} + \text{AgBr}$ .  $\text{C}_{12}\text{H}_6\text{O}_5\text{N}_2\text{ClBr}$  requires  $\text{AgCl} + \text{AgBr}$ , 0.1316 g.).

Similar nitration of 4-chloro-4'-bromo-2-nitrodiphenyl ether gave a product which alone or mixed with the above compound melted at  $165^{\circ}$ .

*4-Bromo-2:2':4'-trinitrodiphenyl Ether.*—(1) 4-Chloro-4'-bromo-2-nitrodiphenyl ether was added to 10 parts of nitric acid ( $d$  1.5) and the resulting solution was heated at  $100^{\circ}$  for 2 hours and then cooled and poured into water. The precipitated solid crystallised from glacial acetic acid in pale yellow, prismatic needles, m. p.  $154^{\circ}$  (Found: Br, 20.1. Calc.: Br, 20.8%). Raiford and Colbert (*loc. cit.*) gave m. p.  $148.5^{\circ}$ . We have found that a specimen kept for some months melts at  $148$ – $149^{\circ}$ . (2) Similar nitration of 4-chloro-4'-bromo-2'-nitrodiphenyl ether gave an identical product.

*4:4'-Dichloro-2:2'-dinitrodiphenyl Ether.*—A solution of 4:4'-dichloro-2-nitrodiphenyl ether in 10 parts of nitric acid ( $d$  1.5) was warmed gently for 10 minutes. The cooled solution was poured into water, and the precipitate crystallised from glacial acetic acid. The dinitro-compound melted at  $154^{\circ}$  (compare Le Fèvre, Saunders, and Turner, J., 1927, 1168).

*4-Chloro-2:2':4'-trinitrodiphenyl Ether.*—(a) 4:4'-Dichloro-2-nitrodiphenyl ether was added to 10 parts of nitric acid ( $d$  1.5), and the solution heated at  $100^{\circ}$  for 2 hours. The whole was cooled and poured into water, and the solid obtained crystallised from glacial acetic acid. It formed yellow prismatic needles, m. p.  $155^{\circ}$ . Raiford and Colbert (*loc. cit.*) describe the compound as forming yellowish plates, m. p.  $154^{\circ}$  (Found: Cl, 10.8. Calc.: Cl, 10.5%).

(b) 4-Chloro-2:2':4'-trinitrodiphenyl ether was also prepared by condensing *p*-chlorophenol with 1-chloro-2:4-dinitrobenzene, the product being treated with cold fuming nitric acid. The solution was gently warmed and poured into water. The precipitate, after recrystallisation, had m. p.  $155^{\circ}$  alone or when mixed with the product from (a).

(c) 4-Chloro-2'-nitrodiphenyl ether, when nitrated in a similar manner, gave a product identical with those from (a) and (b).

*Prolonged Action of Nitric Acid on 2:4-Dichloro- and 2:4-Dibromo-5:2':4'-trinitrodiphenyl Ether.*—The dichloro-ether was heated with 10 parts of nitric acid ( $d$  1.5) for 2 hours at  $100^{\circ}$ . A little hydrogen chloride was slowly evolved. The solution was poured into water,



and the precipitate washed and dried. It had 90% of the weight of the original ether, and melted at 128°, alone or when mixed with the pure trinitro-ether. Similar treatment of the dibromo-ether gave 92% of unchanged ether, m. p. 139—140° alone or mixed with pure ether.

2-Chloro-2'-nitrodiphenyl ether had b. p. 345°, m. p. 47—48°. Roberts and Turner (J., 1925, 127, 1008) gave m. p. 48° (Found : Cl, 14.3. Calc. : Cl, 14.2%).

2-Chloro-2' : 4'-dinitrodiphenyl ether, prepared from *o*-chlorophenol and 1-chloro-2 : 4-dinitrobenzene, crystallised from glacial acetic acid-alcohol in cream-coloured prisms, m. p. 75—76° (Found : Cl, 12.0.  $C_{12}H_7O_5N_2Cl$  requires Cl, 12.05%).

2-Chloro-4 : 2'-dinitrodiphenyl Ether.—2-Chloro-2'-nitrodiphenyl ether was dissolved in 10 parts of nitric acid (*d* 1.4) with warming. The solution was poured into water; the precipitate obtained, after crystallising from glacial acetic acid, had m. p. 126—127° (Found : Cl, 12.0.  $C_{12}H_7O_5N_2Cl$  requires Cl, 12.05%).

2-Chloro-4 : 2' : 4'-trinitrodiphenyl Ether.—A solution of the 4 : 2'-dinitro-ether in 10 parts of nitric acid (*d* 1.5) was heated for 20 minutes at 100° and then poured into water. The resulting precipitate separated from glacial acetic acid in yellow rhombohedra, m. p. 135—136° (Found : Cl, 9.8.  $C_{12}H_6O_7N_3Cl$  requires Cl, 10.5%).

4-Bromo-2-nitrodiphenyl Ether.—A mixture of 6 g. of potassium hydroxide, 0.2 c.c. of water, 9 g. of phenol, and 28 g. of 2 : 5-dibromonitrobenzene was allowed to react for 6 hours under the usual conditions. Although potassium bromide separated, only 14 g. of 4-bromo-2-nitrodiphenyl ether were obtained, as a dark oil, b. p. 228—230°/21 mm. It was found impossible to remove a small quantity of unchanged dibromonitrobenzene (Found : Br, 28.7.  $C_{12}H_8O_3NBr$  requires Br, 27.2%).

Bromination of 4-Bromo-2-nitrodiphenyl Ether.—A solution of 29 g. of this ether and 14.8 c.c. of bromine in 135 c.c. of glacial acetic acid was heated under reflux at 100° until hydrogen bromide was no longer evolved. The solution was poured into water, and the precipitate filtered off. It melted at 94° after crystallisation from glacial acetic acid, and was identical with a specimen of 4 : 4'-dibromo-2-nitrodiphenyl ether obtained by the mononitration of 4 : 4'-dibromodiphenyl ether (Le Fèvre, Saunders, and Turner, *loc. cit.*).

Prolonged Nitration of 4-Bromo-2-nitrodiphenyl Ether.—The ether was dissolved in 10 parts of nitric acid (*d* 1.5), and a clear solution obtained by warming. On pouring the solution into water, and crystallising the precipitate from glacial acetic acid, a product was obtained, m. p. 180—182°. A second similar nitration raised the m. p.

to 191—192°, a third to 195—196°, and a fourth to 196°. The final product did not depress the m. p. of 2 : 4 : 2' : 4'-tetranitrodiphenyl ether. In another experiment, 5 g. of 4-bromo-2-nitrodiphenyl ether were heated with 25 g. of nitric acid (*d* 1.5) for 2 hours at 100°. The gases evolved were absorbed in alkali, and the alkaline solution analysed. It was found that 80% of the bromine originally present had been given off. Pure tetranitrodiphenyl ether was obtained from the nitric acid solution.

*Bromination of 2-Nitrodiphenyl Ether.*—A solution of 20 g. of the ether and 16 g. of bromine in 40 g. of glacial acetic acid was heated under reflux at 100° until the colour of the bromine had disappeared. The solution was poured into alcohol. The solid that separated on standing was crystallised from glacial acetic acid, and then had m. p. 72°. Raiford and Colbert (*loc. cit.*) obtained 4-bromo-2'-nitrodiphenyl ether by a condensation process, and gave m. p. 71°.

*2-Bromo-2' : 4'-dinitrodiphenyl ether*, from *o*-bromophenol and 1-chloro-2 : 4-dinitrobenzene, separated from glacial acetic acid in pale yellow leaflets, m. p. 88—89° (Found : Br, 23.4.  $C_{12}H_7O_5N_2Br$  requires Br, 23.6%).

*Mononitration of 2-Bromo-2' : 4'-dinitrodiphenyl Ether.*—The ether was added to a mixture of 5 parts of glacial acetic acid and 5 parts of nitric acid (*d* 1.5). A clear solution was produced by warming, and after 20 minutes it was poured into water, and the precipitate collected. The 2-bromo-4 : 2' : 4'-trinitrodiphenyl ether crystallised from glacial acetic acid in small yellow needles, m. p. 127—128° (Found : Br, 21.6.  $C_{12}H_6O_7N_3Br$  requires Br, 20.8%).

*2-Bromo-2'-nitrodiphenyl ether*, from *o*-bromophenol and *o*-chloro-nitrobenzene, had b. p. 251°/27 mm. It crystallised from glacial acetic acid-alcohol in yellow prisms, m. p. 49—50° (Found : Br, 27.6.  $C_{12}H_8O_3NBr$  requires Br, 27.2%).

*2-Bromo-4 : 2'-dinitrodiphenyl Ether.*—2-Bromo-2'-nitrodiphenyl ether (3 g.) was added to a mixture of 15 g. of glacial acetic acid and 15 g. of nitric acid (*d* 1.5). The whole was warmed until solution was complete, left for 20 minutes, and poured into water. The product separated from glacial acetic acid in rectangular crystals, m. p. 128° (Found : Br, 24.1.  $C_{12}H_7O_5N_2Br$  requires Br, 23.6%).

*Nitration of 4-Bromo-2' : 4'-dinitrodiphenyl Ether.*—A solution of the ether in 10 parts of nitric acid (*d* 1.5) was warmed for a few minutes and poured into water, and the precipitate crystallised from glacial acetic acid; 4-bromo-2 : 2' : 4'-trinitrodiphenyl ether was then obtained, m. p. 154°.

*4-Chloro-2-nitro-4'-methyldiphenyl ether*, prepared from *p*-cresol and 2 : 5-dichloronitrobenzene, crystallised from alcohol in pale brownish plates, m. p. 99° (Found : Cl, 13.8.  $C_{13}H_{10}O_3NCl$  requires Cl, 13.6%).

An attempt was made to nitrate the ether with concentrated sulphuric acid and potassium nitrate. When the ether was dissolved in the acid, hydrogen chloride was evolved, and on warming at  $100^{\circ}$  a clear solution was obtained, which on cooling and dilution gave white silky needles of 2-nitro-4'-methyldiphenyl ether 4-sulphonic acid, m. p.  $129-130^{\circ}$ . Crystallisation from light petroleum did not affect this m. p. (Found: S, 11.0.  $C_{13}H_{11}O_6NS$  requires S, 10.4%).

*Action of Piperidine on 4-Chloro-2-nitro-4'-methyldiphenyl Ether.*—The ether was heated for an hour at  $100^{\circ}$  with its own weight of piperidine. When the solution was made alkaline, a mixture of 4-chloro-2-nitrophenylpiperidine and unchanged ether was precipitated. The mixture was extracted with 50% sulphuric acid; from the acid extract, on treatment with alkali, the pure chloro-nitrophenylpiperidine was precipitated. In a second experiment, a solution of the ether in excess of piperidine was boiled for several hours, the bulk of the piperidine distilled off, and alkali added; the chloronitrophenylpiperidine which then separated was removed. The filtrate was extracted with benzene until it was colourless, traces of benzene were removed by boiling, and *p*-toluenesulphonyl chloride was added to the heated alkaline solution. After some time, *p*-tolyl *p*-toluenesulphonate separated; after crystallisation from acetic acid-alcohol, it had m. p.  $68^{\circ}$ , alone or when mixed with an authentic specimen.

*4-Chloro-2 : 2'-dinitro-4'-methyldiphenyl Ether.*—4-Chloro-2-nitro-4'-methyldiphenyl ether was dissolved in an ice-cold mixture of 5 parts of glacial acetic acid and 5 parts of nitric acid (*d* 1.5). The solution was heated at  $100^{\circ}$  for an hour, cooled, and poured into water. The precipitate crystallised from acetic acid and alcohol in very pale yellow plates, m. p.  $115^{\circ}$  (Found: Cl, 12.1.  $C_{13}H_9O_5N_2Cl$  requires Cl, 11.5%).

When a solution of the dinitro-ether in nitric acid (*d* 1.5) was heated at  $100^{\circ}$  for an hour, hydrogen chloride was slowly evolved. When the solution was poured into water, a solid was obtained, m. p.  $146-149^{\circ}$ . This could not be separated into definite fractions, but was probably a mixture of unchanged material with 2 : 4 : 2'-trinitro-4'-methyldiphenyl ether.

*4-Chloro-2'-nitro-4'-methyldiphenyl ether*, prepared from 4-chloro-3-nitrotoluene and *p*-chlorophenol, crystallised from alcohol in very pale yellow, irregular, rectangular plates, m. p.  $52^{\circ}$  (Found: Cl, 13.6.  $C_{13}H_{10}O_3NCl$  requires Cl, 13.6%).

When a solution of the ether in 5 parts of glacial acetic acid and 5 parts of nitric acid (*d* 1.5) was heated for an hour at  $100^{\circ}$ , 4-chloro-2 : 2'-dinitro-4'-methyldiphenyl ether was obtained, identical with the product of nitrating the isomeric 2-nitro-ether.

*Action of Piperidine on 4-Chloro-2'-nitro-4'-methyldiphenyl Ether.*—A solution of the ether in its own weight of piperidine was heated for an hour at 100°. When excess of alkali was added to the cooled solution, 2-nitro-4-methylphenylpiperidine separated, m. p. 69°.

*Nitrative Scission of 4-Chloro-2-nitro-4'-methyl- and of 4-Chloro-2'-nitro-4'-methyl-diphenyl Ether.*—The ethers were dissolved in 10 parts of nitric acid (*d* 1.5) at 0°. After 20 minutes, the solutions were poured into water, and the yellow precipitates collected. After crystallisation they both melted at 74–75°, and were pure specimens of 4-chloro-2:6-dinitrophenol.

All the m. p.'s given are corrected.

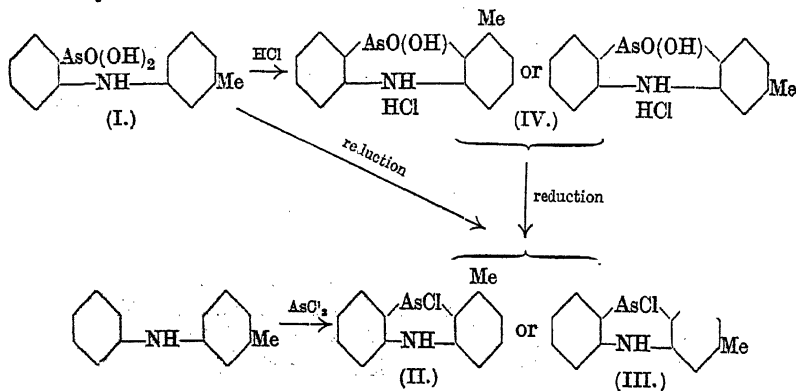
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## CXLII.—10-Chloro-5:10-dihydrophenarsazine and its Derivatives. Part XII. Further Experiments in the Investigation of the 1- and 3-Methyl Derivatives.

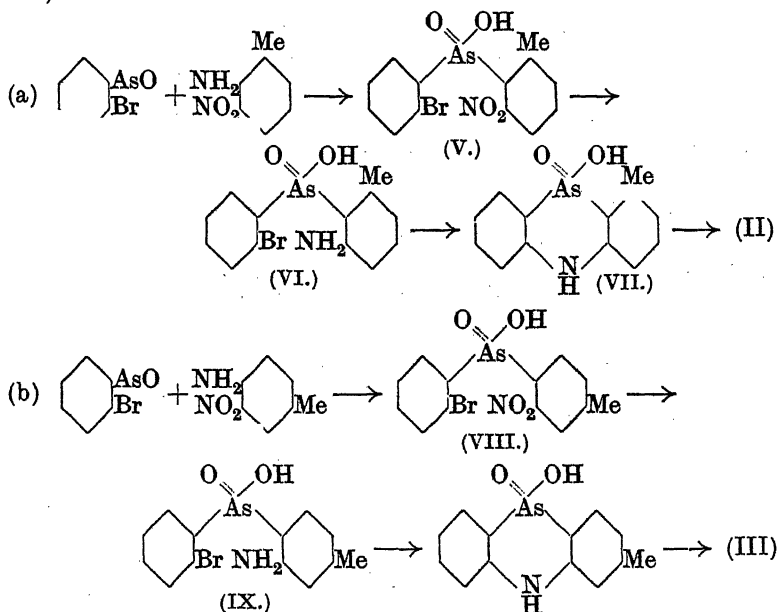
By CHARLES STANLEY GIBSON and JOHN DOBNEY ANDREW JOHNSON.

It was shown in Part VII (J., 1929, 767) that an apparently homogeneous product, which can be either 10-chloro-1-methyl-5:10-dihydrophenarsazine (II) or 10-chloro-3-methyl-5:10-dihydrophenarsazine (III), can be obtained from 3-methyldiphenylamine-6'-arsinic acid (I) either by direct reduction or by conversion first into the homogeneous 1(or 3)-methylphenarsazinic acid hydrochloride (IV) and subsequent reduction of the latter compound. Further, in Part X (J., 1929, 1473), it was proved that the same compound (II) or (III) was the homogeneous condensation product of phenyl-*m*-tolylamine and arsenious chloride.



In order to determine the constitution of the cyclic reduction product obtained from compound (I), substances having the constitutions (II) and (III) were synthesised by methods which should leave no doubt as to their structural formulæ (Part VII, *loc. cit.*). The two substances thus synthesised were, however, indistinguishable and two explanations of this are possible: (1) the two substances may form solid solutions in each other, and (2) one of the rationally synthesised products may be transformed into the other by a rupture of the medial cyclic system, followed by cyclisation in the only other possible way (*loc. cit.*, p. 775).

The synthesis of substances (II) and (III) was attempted by the following series of reactions, which afford as little opportunity as possible of transformation of one into the other; the first stage in each case is analogous to that employed in the first synthesis of 10-chloro-5:10-dihydrophenarsazine (Burton and Gibson, J., 1926, 452):



The advantage of this method of synthesis appeared to be that the final cyclisation process did not involve the arsenic atom, and if the explanation (2, above) of the apparent or real identity of substances (II) and (III) is the rupture of the heterocyclic nucleus, followed by cyclisation in a different way—both of which processes involve the arsenic atom—there was a reasonable hope that the syntheses would be accomplished without intramolecular change.

The series of reactions (b) was readily accomplished, the intermediate substances, 2'-bromo-2-nitro-4-methyldiphenylarsinic acid (VIII) and 2'-bromo-2-amino-4-methyldiphenylarsinic acid (IX) being highly crystalline substances of undoubted purity. The 10-chloro-3-methyl-5:10-dihydrophenarsazine thus rationally synthesised was indistinguishable from either of the previously rationally synthesised products and from the homogeneous products obtained by the methods mentioned above.

Unfortunately, the proposed synthesis of 10-chloro-1-methyl-5:10-dihydrophenarsazine by the series of reactions (a) could not be accomplished. 2'-Bromo-2-nitro-6-methyldiphenylarsinic acid (V) was prepared, but the reduction product could not be purified and an attempt to convert this crude material into (II) was unsuccessful.

Although the immediate object of this part of these investigations has not been accomplished, it may be that 10-chloro-3-methyl-5:10-dihydrophenarsazine has now been definitely synthesised. Before, however, the constitution of the 10-chloro-1(or 3)-methyl-5:10-dihydrophenarsazine obtained in the above-mentioned reactions can be definitely stated, 10-chloro-1-methyl-5:10-dihydrophenarsazine must be synthesised in an unequivocal manner: the balance of evidence, however, appears to be in favour of its being the 3-methyl compound.

The present work indicates that possibly false conclusions may be drawn as to the constitution of the product of a reaction which may give rise to one of two substances when this proves to be identical with one synthesised product and is not compared with the other synthesised isomeric substance. This problem is being investigated in different directions.

#### EXPERIMENTAL.

*o*-Bromophenylarsenious oxide is most conveniently prepared by passing carbon dioxide into a solution of pure *o*-bromophenyldichloroarsine (Burton and Gibson, J., 1926, 457; Kalb, *Annalen*, 1921, 423, 39) in dilute aqueous sodium hydroxide, warmed if necessary. The colourless oxide is filtered off, washed with water, and dried over potassium hydroxide under reduced pressure; it is thus obtained as a fine colourless powder readily soluble in alkali hydroxide solutions.

2'-Bromo-2-nitro-4-methyldiphenylarsinic Acid (VIII).—Finely powdered and sieved 3-nitro-*p*-toluidine (7.6 g.) in hydrochloric acid (40 c.c.) and water (125 c.c.) was diazotised with sodium nitrite (3.8 g.) in water (9 c.c.) below 0°. A solution of *o*-bromophenylarsenious oxide (13.6 g.) in 5*N*-sodium hydroxide (87 c.c.) and water (163 c.c.) to which had been added ammoniacal cupric sulphate

(10% cupric sulphate solution treated with excess of ammonia; 5 c.c.) was then treated slowly at 20° with the diazo-solution without external cooling, the mixture being mechanically stirred. After one hour, the liquid was heated to boiling, treated with decolorising charcoal, and filtered. The filtrate was saturated with carbon dioxide to precipitate unchanged *o*-bromophenylarsenious oxide and, after filtration, carefully acidified with concentrated hydrochloric acid. The amorphous yellow acid which was precipitated could not be crystallised directly and was converted into its sodium salt by dissolving it in warm 20% aqueous sodium hydroxide and cooling the solution. The buff-yellow sodium salt was filtered off, washed with 20% aqueous sodium hydroxide and dissolved in water, and the solution acidified with hydrochloric acid. The almost colourless acid was recrystallised from slightly diluted acetic acid (charcoal) and obtained in colourless needles (4.33 g.), m. p. 252—254° (decomp. after slight softening) (Found: As, 19.2.  $C_{13}H_{11}O_4NBrAs$  requires As, 18.7%). The ammonium salt crystallises from solution in concentrated aqueous ammonia in characteristic, colourless, rhomb-shaped plates.

*2'-Bromo-2-amino-4-methyldiphenylarsinic Acid (IX).*—A hot solution of the preceding acid (5.95 g.) in sodium hydroxide solution (1.5 g. in 30 c.c.) was added to a boiling suspension of ferrous hydroxide [ferrous sulphate crystals (25 g.), water (75 c.c.), and sodium hydroxide solution (25%, 30 c.c.)], and the mixture boiled for 15 minutes and filtered. The filtrate was carefully acidified with concentrated hydrochloric acid; the precipitated acid, recrystallised from slightly diluted acetic acid (charcoal), was obtained in colourless needles (3.9 g.), decomposing vigorously at 264—265° after previous darkening from about 240° (Found: As, 20.7.  $C_{13}H_{13}O_2NBrAs$  requires As, 20.3%). This acid in contradistinction to the nitro-acid is soluble in cold concentrated hydrochloric acid.

*Cyclisation of 2'-bromo-2-amino-4-methyldiphenylarsinic acid.* A mixture of the preceding acid (3.08 g.), potassium carbonate (1.22 g.), amyl alcohol (22 c.c.), and a trace of copper powder was boiled for 15 hours, volatile substances then being removed by steam distillation, the aqueous solution filtered, and the filtrate acidified. The liquid filtered very slowly from the precipitated gelatinous discoloured acid. After being washed with water and dried as far as possible on the filter, the acid was dissolved in a mixture of alcohol and concentrated hydrochloric acid, to which a trace of iodine was added, and the solution was saturated with sulphur dioxide. The discoloured yellow solid was filtered off, dried over potassium hydroxide under reduced pressure, and crystallised from benzene (charcoal). After one crystallisation it had m. p. 215—216° after previous

softening from about  $211^{\circ}$ , and a further crystallisation gave 10-chloro-3-methyl-5:10-dihydrophenarsazine, m. p.  $215-216.5^{\circ}$ ; the yield was small (Found: Cl, 12.3. Calc.: Cl, 12.2%).

*2'-Bromo-2-nitro-6-methyldiphenylarsinic Acid* (V).—This was prepared in a similar manner to that employed for the isomeric acid (VIII), 3-nitro-*o*-toluidine being used instead of 3-nitro-*p*-toluidine. The crude acid was purified by direct crystallisation from slightly diluted acetic acid, from which it separated in almost colourless, small plates. When recrystallised from the same medium, it was obtained in pale yellow plates, softening at  $226^{\circ}$ , darkening and finally decomposing at  $237-239^{\circ}$ ; yield 29% (Found: As, 19.0.  $C_{13}H_{11}O_4NBrAs$  requires As, 18.7%). The sodium salt separates from a solution of the acid in warm 20% aqueous sodium hydroxide in colourless small plates.

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### CXLIH.—*ortho*- and meta-Derivatives of Simple Alkyl Phenyl Ketones.

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IN connexion with a part of an extended investigation of certain types of organic arsenical compound it has been necessary to review our knowledge of derivatives of aceto-, propio-, and *n*-butyrophenones required as starting materials. In certain cases, the published methods of preparation were not suitable for our purpose and, in others, the compounds as described were apparently not pure. This preliminary investigation was, of necessity, somewhat prolonged and entailed the preparation of derivatives not hitherto described.

The first compounds required were the *o*- and *m*-amino-derivatives of the above ketones and their preparation was carried out in the same way in all cases. Each of these ketones, on nitration, yields a mixture of the *o*- and *m*-nitro-compounds, from which the *m*-compound is easily separated and obtained pure, leaving an uncrystallisable oil (crude *o*-nitro-ketone) which is chiefly the *o*-compound containing some of the *m*-isomeride. The pure *m*-nitro-ketone is reduced to the corresponding amino-compound, which can be easily obtained in a state of purity. The crude *o*-nitro-ketone on reduction yields a mixture of the *o*- and the *m*-amino-ketone. From this mixture, the *o*-amino-ketone is



separated by steam distillation; in every case, the *m*-isomeride is much less volatile in steam than the *o*-compound, which can thus be readily obtained pure.

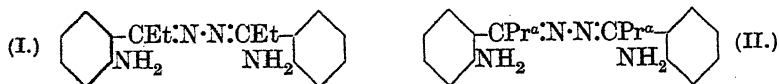
*o*-Aminoacetophenone has now been obtained as a pale yellow, crystalline solid, m. p. 20°. *m*-Bromoacetophenone has m. p. 7—8°; it yields 3 :  $\omega$ -dibromoacetophenone on direct bromination and 5-bromo-2-nitroacetophenone on nitration.

*m*-Aminopropiophenone does not yield a semicarbazone under the same conditions as the *o*-compound. The reaction between *o*-aminopropiophenone and semicarbazide hydrochloride, under the conditions described in the experimental portion, besides giving the semicarbazone, yields another product which is mentioned below. *o*-Bromopropiophenone, when brominated in acetic acid solution, yields 2 :  $\alpha$ -dibromopropiophenone.

*n*-Butyrophenone (*n*-propyl phenyl ketone), prepared from *n*-butyryl chloride by the Friedel-Crafts reaction, has m. p. 13° (compare Morgan and Hickinbottom, J., 1921, **119**, 1882). *o*-Bromobutyrophenone on bromination yields first 2 :  $\alpha$ -dibromobutyrophenone and then 2 :  $\alpha$  :  $\alpha$ -tribromobutyrophenone. Analysis of the latter compound and of 4 :  $\alpha$ -dibromobutyrophenone—prepared from bromobenzene and  $\alpha$ -bromobutyryl chloride by the Friedel-Crafts reaction—indicated the great tendency of these compounds to lose hydrogen bromide. 4-Chloro- $\alpha$ -bromobutyrophenone was, however, isolated in the crystalline state from chlorobenzene and  $\alpha$ -bromobutyryl chloride by the Friedel-Crafts reaction. Like *m*-aminopropiophenone, *m*-aminobutyrophenone does not yield a semicarbazone under the usual conditions. The reaction between *o*-aminobutyrophenone and semicarbazide hydrochloride is discussed below.

With the exceptions noted above, there is little difficulty in isolating the semicarbazones of many of the compounds described and these may prove useful for identification purposes. The reactions, however, between *o*-aminopropiophenone and semicarbazide and between the latter compound and *o*-amino-*n*-butyrophenone need special comment. In isolating the semicarbazone of *o*-aminopropiophenone, it was noticed that the crude substance was contaminated with a bright yellow substance the quantity of which was increased when the reaction was prolonged and especially when the mixture was heated. A yellow substance only was obtained when *o*-amino-*n*-butyrophenone was treated with semicarbazide hydrochloride under the usual conditions, and the yield, again, of this product was increased when the reaction mixture was heated. The two yellow substances resembled each other very closely, both crystallising in yellow needles; that obtained from *o*-amino-

propio-phenone had m. p. 130° and that from *o*-amino-*n*-butyro-phenone had m. p. 135°, this being obtained the more easily. The latter compound had the empirical formula  $C_{10}H_{13}N_2$  and the molecular weight determination by the method of Rast indicated that this was half the molecular formula. It soon became evident that the two compounds were ketazines, that from *o*-aminopropio-phenone being *ethyl-o-aminophenylketazine* (I) and that from *o*-amino-*n*-butyrophenone being *n-propyl-o-aminophenylketazine* (II).



The ease of formation of these substances seems unusual, ketazines being generally formed either by the action of hydrazine on ketones or by heating the semicarbazones to a moderately high temperature (Scholtz, *Ber.*, 1896, **29**, 610; Borsche, *Ber.*, 1901, **34**, 4301; Bruining, *Rec. trav. chim.*, 1922, **41**, [ii], 655), ammonia and hydrazodicarbonimide being formed during the decomposition. An attempt to prepare substance (I) by heating *o*-aminopropio-phenonesemicarbazone above its melting point was unsuccessful, although the formation of a yellow material and evolution of ammonia were noticed. An attempt to prepare methyl-*o*-aminophenylketazine by the action of semicarbazide hydrochloride on *o*-aminoacetophenone in a similar manner to that described above led only to the isolation of the semicarbazone.

#### EXPERIMENTAL.

The nitration of acetophenone has been extensively studied by Morgan and Moss (*J. Soc. Chem. Ind.*, 1923, 461T). For the present work, acetophenone in lots of 30 c.c. was run slowly into stirred nitric acid (*d* 1.50), 140 c.c. being used each time and the temperature kept below 0°. After  $\frac{1}{2}$  hour, the product was poured on ice, and the crystalline *m*-nitroacetophenone separated by filtration. From the filtrate, made alkaline with sodium carbonate and hydroxide, the crude *o*-nitroacetophenone (containing some of the *m*-isomeride) was extracted with ether, the extract was washed with water and dried with calcium chloride, and the ether evaporated. To this crude *o*-nitroacetophenone was added the oily residue resulting from the evaporation of the alcoholic mother-liquor from the recrystallisation of the *m*-nitroacetophenone.

The pure *m*-nitroacetophenone was reduced under substantially the same conditions as described by Morgan and Moss. After recrystallisation from alcohol, *m*-aminoacetophenone was obtained in pale yellow plates, m. p. 98—99° (Morgan and Moss give 92—93°).

*m*-Aminoacetophenonesemicarbazone crystallises from water in

colourless prisms, m. p.  $196^{\circ}$  (decomp.) (Found : N, 29.3.  $C_9H_{12}ON_4$  requires N, 29.2%), and *m*-*p*-toluenesulphonamidoacetophenone from alcohol in colourless needles, m. p.  $130^{\circ}$  (Found : N, 4.9.  $C_{15}H_{15}O_3NS$  requires N, 4.85%).

The crude *o*-nitroacetophenone was reduced with tin and hydrochloric acid as described by Morgan and Moss. The resulting mixture was made strongly alkaline with sodium hydroxide and submitted to steam distillation. The *o*-aminoacetophenone in the distillate was extracted with ether, dried with calcium chloride, and recovered; it had b. p.  $130.5^{\circ}/14$  mm.,  $124^{\circ}/10$  mm., m. p.  $20^{\circ}$  (compare Morgan and Moss, *loc. cit.*). The pure ketone is almost colourless.

*o*-Aminoacetophenonesemicarbazone crystallises from alcohol in colourless plates, m. p.  $290^{\circ}$  (decomp.) (Found : N, 29.8.  $C_9H_{12}ON_4$  requires N, 29.2%). The *p*-toluenesulphonyl derivative crystallises from alcohol in colourless hexagonal plates, m. p.  $148^{\circ}$  (Found : N, 4.9.  $C_{15}H_{15}O_3NS$  requires N, 4.85%).

From 180 g. of acetophenone were obtained 40 g. of pure *o*-aminoacetophenone and 65 g. of pure *m*-aminoacetophenone.

To obtain *o*-bromoacetophenone (compare Meisenheimer, Zimmermann, and Kummer, *Annalen*, 1926, **446**, 205), *o*-aminoacetophenone (40 g.) was dissolved in hydrobromic acid (36%, 122 c.c.) and water (120 c.c.) and diazotised with a solution of sodium nitrite (21.2 g.) in water (36 c.c.) below  $0^{\circ}$ . The diazotised solution was treated with a solution in hydrobromic acid ( $d$  1.49, 100 c.c.) of cuprous bromide made by reducing copper sulphate crystals (54.2 g.) in water (180 c.c.), mixed with potassium bromide (27.2 g.) dissolved in water (63 c.c.), with sulphur dioxide. After heating for some time on the water-bath, the *o*-bromoacetophenone was removed by steam distillation, extracted from the distillate with ether, washed successively with dilute sodium hydroxide solution, dilute hydrochloric acid, and water, dried with calcium chloride, and recovered. On distillation under reduced pressure it was obtained as a pale yellow liquid, b. p.  $112^{\circ}/10$  mm., which did not solidify above  $-16^{\circ}$ . Yield, 80%.

*o*-Bromoacetophenonesemicarbazone crystallised from alcohol in colourless prisms, m. p.  $177^{\circ}$  (Found : N, 16.7.  $C_9H_{10}ON_3Br$  requires N, 16.4%).

*m*-Bromoacetophenone, obtained from *m*-aminoacetophenone as *o*-bromoacetophenone from *o*-aminoacetophenone, is a pale yellow oil, b. p.  $127.5^{\circ}/14$  mm. and  $131^{\circ}/16$  mm., which solidifies to an almost colourless, crystalline solid, m. p.  $7-8^{\circ}$ . Yield, 54% (Found : Br, 40.5.  $C_8H_7OBr$  requires Br, 40.15%). On oxidation with sodium hypobromite it was converted into *m*-bromobenzoic acid, m. p.  $155^{\circ}$ .

*m*-Bromoacetophenonesemicarbazone crystallised from alcohol in colourless needles, m. p. 232—233° (decomp.) (Found : N, 16.3.  $C_9H_{10}ON_3Br$  requires N, 16.4%).

5-Bromo-2-nitroacetophenone was obtained by adding *m*-bromoacetophenone (10 g.) to well-stirred nitric acid (*d* 1.50, 70 c.c.) below 0° and pouring the mixture on ice; the solid produced crystallised from alcohol (charcoal) in almost colourless needles, m. p. 98° (Found : N, 5.8.  $C_8H_6O_3NBr$  requires N, 5.7%). It gave 5-bromo-2-nitrobenzoic acid, m. p. 138—140°, on oxidation with sodium hypobromite.

3 :  $\omega$ -Dibromoacetophenone.—*m*-Bromoacetophenone (12.2 g.), dissolved in acetic acid (50 c.c.), was treated with bromine (3.08 c.c., 1 mol.). On heating on the water-bath, hydrogen bromide was evolved and the liquid became colourless. It was then poured into water and the 3 :  $\omega$ -dibromoacetophenone was extracted with ether, washed with dilute sodium hydroxide solution and then with water, dried with calcium chloride, recovered, and distilled under reduced pressure, some unchanged material distilling first. The dibromo-ketone, obtained in 40% yield, had b. p. 172—174°/14 mm., solidified on cooling, and crystallised from ligroin (b. p. 60—80°) in long colourless needles, m. p. 51° (Found : Br, 57.1.  $C_8H_6OBr_2$  requires Br, 57.5%). By oxidation with sodium hypobromite it was converted into *m*-bromobenzoic acid, m. p. 154°.

3 :  $\omega$ -Dibromoacetophenonesemicarbazone crystallises in clusters of flattened needles, m. p. 163—164° (decomp.) (Found : N, 13.05.  $C_9H_9ON_3Br_2$  requires N, 12.55%).

*The Nitration of Propiophenone*.—This was carried out exactly similarly to that of acetophenone and the products were also worked up similarly. The *m*-nitropropiophenone crystallises in pale yellow needles, m. p. 98—100°, and on oxidation with potassium permanganate is converted into *m*-nitrobenzoic acid (compare, however, Comanducci and Pescitelli, *Gazzetta*, 1906, 36, ii, 787).

The reduction of *m*-nitropropiophenone was carried out with iron turnings and acetic acid, and the product worked up in the usual manner. *m*-Aminopropiophenone was obtained as a pale yellow oil, b. p. 168—169°/15 mm., which solidified to a yellow solid, m. p. 42° (Found : C, 73.3; H, 7.5.  $C_9H_{11}ON$  requires C, 72.5; H, 7.4%). The yield is variable and may be as high as 60%; in some cases a large quantity of a resinous mass remained after the first distillation.

*m*-p-Toluenesulphonamidopropiophenone crystallised from alcohol in colourless needles, m. p. 97° (Found : N, 4.7.  $C_{16}H_{17}O_3NS$  requires N, 4.6%).

The reduction of the crude *o*-nitropropiophenone with tin and

hydrochloric acid was carried out in the same manner as for the crude *o*-nitroacetophenone. The *o*-aminopropiophenone was isolated by steam distillation and crystallised from the distillate in pale yellow plates, m. p.  $46^{\circ}$  (compare Auwers and Duesberg, *Ber.*, 1920, 53, 1208). From 290 g. of propiophenone were obtained in a state of purity 35 g. of *o*-aminopropiophenone and 73 g. of *m*-aminopropiophenone.

*o*-Aminopropiophenonesemicarbazone, when prepared in the usual manner in the cold, crystallises from alcohol in colourless prisms, m. p.  $190^{\circ}$  (decomp.) (Found: N, 27.3.  $C_{10}H_{14}ON_4$  requires N, 27.2%). When the solution of the reacting substances is heated, the semicarbazone obtained is mixed with the ketazine (see below). *o*-p-Toluenesulphonamidopropiophenone crystallises from alcohol in colourless prisms; it does not appear to have a definite melting point, softening at about  $125^{\circ}$  and then decomposing over a considerable range (Found: N, 4.6.  $C_{16}H_{17}O_3NS$  requires N, 4.6%).

*o*-Bromopropiophenone, prepared from *o*-aminopropiophenone in the same way as the bromoacetophenones from the corresponding amino-compounds, was obtained as a pale yellow oil, b. p.  $125^{\circ}/12$  mm., which does not solidify above  $-16^{\circ}$ ; yield, 75% (Found: Br, 37.3.  $C_9H_9OBr$  requires Br, 37.5%). *o*-Bromopropiophenonesemicarbazone crystallises from alcohol in colourless plates, m. p.  $182^{\circ}$  (Found: N, 15.7.  $C_{10}H_{12}ON_3Br$  requires N, 15.55%).

On bromination of *o*-bromopropiophenone in acetic acid under similar conditions to those described above, what was probably *o*: $\alpha$ -dibromopropiophenone was formed. This was obtained as a pale yellow liquid, b. p.  $154$ – $155^{\circ}/12$  mm., which solidified and crystallised in flat prisms with pyramidal ends, m. p.  $38$ – $39^{\circ}$ ; yield, 75% (Found: Br, 54.0.  $C_9H_8OBr_2$  requires Br, 54.7%). It gave, on oxidation with potassium permanganate, *o*-bromobenzoic acid, m. p.  $147^{\circ}$ .

*m*-Bromopropiophenone, prepared in the usual manner from *m*-aminopropiophenone, is a yellow liquid, b. p.  $143^{\circ}/18$  mm., which sets to a pale yellow solid, m. p.  $36^{\circ}$ ; yield, 52% (Found: Br, 36.7.  $C_9H_9OBr$  requires Br, 37.5%). *m*-Bromopropiophenonesemicarbazone crystallises from alcohol in colourless needles, m. p.  $180^{\circ}$  (Found: N, 15.6.  $C_{10}H_{12}ON_3Br$  requires N, 15.55%).

*n*-Butyrophenone was obtained in 66% yield by the action of *n*-butyryl chloride on benzene in the presence of aluminium chloride. It has m. p.  $13^{\circ}$ . It was nitrated in the manner above described for the analogous compounds (compare Morgan and Hickinbottom, *J.*, 1921, 119, 1882) and the products were worked up in the usual manner. *m*-Nitro-*n*-butyrophenone had m. p.  $62$ – $63^{\circ}$  when recrystallised from alcohol (almost colourless plates) and was

obtained in 42% yield. *m*-Nitro-*n*-butyrophenonesemicarbazone crystallised from alcohol in pale yellow needles, m. p. 166—167° (Found: N, 22.8.  $C_{11}H_{14}O_3N_4$  requires N, 22.4%). The constituents of the crude *o*-nitro-*n*-butyrophenone could not be separated by fractional distillation under reduced pressure.

Pure *m*-nitro-*n*-butyrophenone was reduced with iron turnings and acetic acid in the manner already described, and the reaction product worked up in the usual manner. *m*-Amino-*n*-butyrophenone is a pale yellow liquid, b. p. 179—180°/16 mm., which sets to a yellow solid, m. p. 27—28°. *m*-*p*-Toluenesulphonamido-*n*-butyrophenone crystallises from somewhat diluted alcohol in colourless needles, m. p. 70° (Found: N, 4.3.  $C_{17}H_{19}O_3NS$  requires N, 4.4%).

The crude *o*-nitro-*n*-butyrophenone was reduced with tin and hydrochloric acid and the reduction product was worked up in a similar manner to that employed for the crude *o*-nitroacetophenone, the *o*-amino-*n*-butyrophenone, unlike the corresponding *m*-compound, being volatile in steam. *o*-Amino-*n*-butyrophenone crystallises from alcohol in colourless plates, m. p. 45°; it has b. p. 153°/16 mm. (Found: N, 8.9.  $C_{10}H_{13}ON$  requires N, 8.6%). From 375 g. of *n*-butyrophenone were obtained 55 g. of pure *o*-amino-*n*-butyrophenone and 85 g. of pure *m*-amino-*n*-butyrophenone.

*o*-*p*-Toluenesulphonamido-*n*-butyrophenone crystallises from alcohol in colourless rhombic plates, m. p. 110° (Found: N, 4.35.  $C_{17}H_{19}O_3NS$  requires N, 4.4%).

*o*-Bromo-*n*-butyrophenone, prepared from the *o*-amino-compound in the usual way, is a very pale yellow oil, b. p. 143°/16 mm., which does not solidify above -16°. The yield is 68% (Found: Br, 34.5.  $C_{10}H_{11}OBr$  requires Br, 35.2%).

*o*-Bromo-*n*-butyrophenonesemicarbazone crystallises from alcohol in colourless needles, m. p. 172° (Found: N, 15.15.  $C_{11}H_{14}ON_3Br$  requires N, 15.45%).

What is presumably *o*: $\alpha$ -dibromo-*n*-butyrophenone was obtained by the bromination of *o*-bromo-*n*-butyrophenone in acetic acid solution with bromine (1 mol.). It is a pale yellow oil, b. p. 172°/16 mm., which darkens in the air. It does not solidify above -16° (Found: Br, 51.4.  $C_{10}H_{10}OBr_2$  requires Br, 52.2%). When oxidised with potassium permanganate it is converted into *o*-bromobenzoic acid, m. p. 148°.

When *o*-bromo-*n*-butyrophenone was brominated with bromine (3 mols.), some of the latter remained unabsorbed and was evaporated. The product was poured into water, extracted with ether, and the ether evaporated. The solid residue was crystallised by allowing its solution in alcohol to evaporate slowly and was obtained

in colourless plates, m. p. 27–28° (Found : Br, 61.3.  $C_{10}H_9OBr_3$  requires Br, 62.3%). The substance, probably *o*: $\alpha$ : $\alpha$ -tribromo-*n*-butyrophenone, was not readily oxidised by the ordinary methods.

*m*-Bromo-*n*-butyrophenone, obtained from *m*-amino-*n*-butyrophenone, is a pale yellow liquid, b. p. 152°/20 mm. It solidifies to an almost colourless solid, m. p. 9–10°; yield, 41% (Found : Br, 34.2.  $C_{10}H_{11}OBr$  requires Br, 35.2%). Its semicarbazone crystallises from alcohol in colourless prisms, m. p. 158° (Found : N, 15.4.  $C_{11}H_{14}ON_3Br$  requires N, 15.45%).

*p*-Chloro- $\alpha$ -bromo-*n*-butyrophenone was obtained by treating  $\alpha$ -bromobutyryl chloride (46.4 g.) with chlorobenzene (84.4 g.) in the presence of aluminium chloride (36 g.) and carbon disulphide (46 c.c.). After the vigorous reaction had ceased, the mixture was boiled for 2 hours, poured into water, and extracted with ether and the extract was evaporated after being washed and dried. The product was distilled and had b. p. 162°/14 mm.; yield, 66%. It crystallised from alcohol in colourless rectangular plates, m. p. 43° (Found : 0.3928 g. gave 0.4960 g. of mixed silver halides.  $C_{10}H_{10}OClBr$  requires 0.4974 g.). On oxidation with potassium permanganate, *p*-chlorobenzoic acid, m. p. 236°, was obtained.

On attempting to prepare *p*: $\alpha$ -dibromo-*n*-butyrophenone by the same method, an almost colourless liquid having b. p. 180°/15 mm. and containing 47.1% of bromine ( $C_{10}H_{10}OBr_2$  requires Br, 52.2%) was obtained in a yield of 79%. The substance obtained in 58% yield by the bromination of *m*-bromo-*n*-butyrophenone was a yellow oil, b. p. 180°/18 mm. (Found : Br, 49.9%).

Both of these substances darken rapidly on standing and the low bromine content is due to partial decomposition with elimination of hydrogen bromide from the side chain.

*n*-Propyl-*o*-aminophenylketazine (II).—A mixture of *o*-amino-*n*-butyrophenone (3.4 g.), alcohol (22 c.c.), semicarbazide hydrochloride (2.7 g.), sodium acetate (6 g.), and water (22 c.c.) was kept for several days; yellow needles then separated. The substance, which was formed more rapidly when the mixture was heated on the water-bath, crystallised from alcohol, in which it was readily soluble, in yellow needles, m. p. 135° (Found : C, 74.6; H, 8.0; N, 17.4; *M*, 328.  $C_{20}H_{26}N_4$  requires C, 74.5; H, 8.1; N, 17.4%; *M*, 322).

The compound is insoluble in water and dissolves to a colourless solution in dilute hydrochloric acid, from which, on being made alkaline, an oil, probably *o*-amino-*n*-butyrophenone, is precipitated.

*Ethyl-o*-aminophenylketazine (I).—A mixture of *o*-aminopropiophenone (3.3 g.), semicarbazide hydrochloride (2.7 g.), sodium acetate (6 g.), alcohol (22.5 c.c.), and water (22.5 c.c.) was boiled

for several days; the yellow ketazine then separated together with some colourless semicarbazone. The mixture of solids was boiled with a little alcohol to dissolve the more soluble ketazine, and the solution filtered. The ketazine which crystallised from the filtrate was pure after one further crystallisation from alcohol, forming yellow needles, m. p.  $130^{\circ}$  (Found: C, 73.8; H, 7.8; N, 18.8.  $C_{18}H_{22}N_4$  requires C, 73.5; H, 7.5; N, 19.05%). Like compound (II), it dissolves to a colourless solution in hydrochloric acid; when this solution is made alkaline, an oil, probably *o*-aminopropiophenone, is precipitated.

On heating *o*-aminopropiophenonesemicarbazone for 2 hours at  $230$ – $240^{\circ}$ , a yellow resinous material was produced, ammonia having been evolved. It was not possible to separate any of the expected ketazine from the solid product.

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#### CXLIV.—*The Synthesis of Glucosides. Part IV.* *Alizarin Glucoside.*

By ALEXANDER ROBERTSON.

By the interaction of tetra-acetyl- $\alpha$ -glucosidyl bromide and alizarin in the presence of quinoline and silver oxide, Takahashi (*J. Pharm. Soc. Japan*, 1925, 525, 4) prepared the tetra-acetyl glucoside of alizarin, which on deacetylation with alkali yielded a mono-glucoside, m. p.  $230$ – $231^{\circ}$ . Glaser and Kahler (*Ber.*, 1927, 60, 1349), using the acetone-alkali method, seem to have isolated the same tetra-acetyl glucoside, but on deacetylation by means of methyl-alcoholic ammonia they obtained alizarin and a red compound which they considered was the 1:2-diglucoside of 9:10-diamino-1:2:9:10-tetrahydroxyanthracene and was converted by cold hydrochloric acid into 1:2-diglucoalizarin, m. p.  $214^{\circ}$ . The production of a diglucoside in this manner was thought to be highly improbable, and, moreover, would restrict the use of this convenient method of deacetylation. In addition, the results were complicated by the fact that Fischer's method for the preparation of  $\alpha$ -glucosides depends on the use of quinoline (*Ber.*, 1916, 49, 2813). The experiments described in this communication were therefore undertaken.

Zemplén and Müller (*Ber.*, 1929, 62, 2107), using Takahashi's method, have confirmed the results of this investigator. They also found that deacetylation of the tetra-acetyl glucoside as described by Glaser and Kahler gave a red compound of variable composition which on treatment with warm aqueous-alcoholic hydrochloric acid



afforded alizarin monoglucoside identical with that, m. p. 236—237°, obtained by deacetylation with alkali. The experimental results described below agree with the observations of Zemplén and Müller. A convenient procedure for the preparation of the tetra-acetyl glucoside by the acetone-alkali method is described (compare Glaser and Kahler, *loc. cit.*). Since acetylation of alizarin glucoside prepared by either method of hydrolysis and of the tetra-acetyl derivative gave the same penta-acetyl compound, it follows that migration of the glucose residue does not occur.

The fact that the red compound is not instantaneously decomposed by warm dilute acetic acid renders it unlikely that the substance is a simple ammonium salt. In support of this it may be noted that alizarin glucoside is liberated from its sodium salt by cold dilute acetic acid. Deacetylation of *O*-tetra-acetyl-2- $\beta$ -glucosidoxyanthraquinone (compare Müller, *Ber.*, 1929, 62, 2793) with methyl-alcoholic ammonia gave 2- $\beta$ -glucosidoxyanthraquinone identical with that obtained by hydrolysis with alkali.

Previous investigators (Takahashi, *loc. cit.*; Glaser and Kahler, *loc. cit.*; Zemplén and Müller, *loc. cit.*) have suggested that the glucose residue of the tetra-acetyl glucoside of alizarin is attached at the 2-position. This conclusion was based on the well-known fact that in compounds like alizarin the hydroxyl group in the *o*-position to carbonyl is difficult to alkylate. Attempts to confirm this structure by the aid of boroacetic anhydride gave unsatisfactory results (compare Robertson and Waters, J., 1929, 2239). Although the addition of the glucoside or its acetyl compound to a solution of the reagent in acetic anhydride gave a red coloration indicating the formation of a boroacetate, a solid derivative could not be isolated; the red solutions became yellow on addition of water. The isolation of 1-methyl alizarin as a product of the hydrolysis of *O*-tetra-acetyl-2- $\beta$ -glucosidoxy-1-methoxyanthraquinone (I) finally afforded conclusive proof of the constitutions of (I) and of alizarin glucoside; deacetylation of (I) gave the glucoside of 1-methyl alizarin.

Acetylation of the amorphous condensation product of *O*-hepta-acetylmaltosidyl bromide and alizarin gave a crystalline *O*-octa-acetyl maltoside, not identical with the octa-acetyl derivative of ruberythric acid.

The hydroxyxanthone glucosides (Robertson and Waters, *loc. cit.*) are readily decomposed by boiling 10% aqueous sodium hydroxide and in this respect resemble the compounds described in this communication.

#### EXPERIMENTAL.

2- $\beta$ -Glucosidoxyanthraquinone.—*O*-Tetra-acetyl- $\alpha$ -glucosidyl bromide (8.2 g.) was added to a solution of 2-hydroxyanthraquinone

(6 g.) and potassium hydroxide (1.2 g.) in acetone (60 c.c.) and water (20 c.c.). The mixture was kept at room temperature for 16 hours and 12% aqueous potassium hydroxide (10 c.c.) and a further quantity of bromide (8.2 g.) were then added. After 24 hours, the reaction mixture was acidified with acetic acid, and on addition of water (300 c.c.) the tetra-acetyl glucoside (mixed with 2-hydroxy-anthraquinone) separated. Repeated crystallisation from alcohol gave the substance (3.5 g.) in almost colourless, rectangular plates, m. p. 168° (Müller, *loc. cit.*, gives m. p. 164°) (Found in material dried at 100°: C, 60.6; H, 5.0. Calc. for  $C_{28}H_{26}O_{12}$ : C, 60.5; H, 4.7%).

The tetra-acetyl derivative (2 g.), suspended in warm methyl alcohol (80 c.c.), was treated with 10% aqueous sodium hydroxide (16 c.c.) at 60° for 5 minutes. The cooled mixture slowly deposited 2- $\beta$ -glucosidoxyanthraquinone (1 g.), which crystallised from dilute alcohol in pale yellow needles containing  $1H_2O$ , m. p. 248—249° (Found: C, 59.5; H, 5.3.  $C_{20}H_{18}O_8 \cdot H_2O$  requires C, 59.4; H, 5.0%. Found in material dried at 110° in a high vacuum for 2 hours: C, 62.2; H, 4.7.  $C_{20}H_{18}O_8$  requires C, 62.2; H, 4.7%). The compound tends to separate from warm dilute alcohol as a pale yellow gel which gradually crystallises. It is moderately easily soluble in warm water and sparingly soluble in hot alcohol. Acetylation with acetic anhydride and sodium acetate gave the tetra-acetyl derivative, m. p. 168°. In boiling 10% aqueous sodium hydroxide the glucoside decomposes with the formation of the red sodium salt of 2-hydroxy-anthraquinone. It is readily hydrolysed by emulsin and by warm 15% hydrochloric acid to glucose and the anthraquinone.

Deacetylation of the tetra-acetyl glucoside by means of methyl-alcoholic ammonia during 22 hours at 0° afforded the glucoside in almost theoretical yield, m. p. and mixed m. p. 248—249° after crystallisation from dilute alcohol.

2-O-Tetra-acetyl- $\beta$ -glucosidoxy-1-hydroxyanthraquinone.—A mixture of alizarin (18 g.), potassium hydroxide (2.8 g.), and 50% aqueous acetone (400 c.c.) was agitated for  $\frac{1}{4}$  hour to ensure the formation of potassium alizarate. A solution of O-tetra-acetyl- $\alpha$ -glucosidyl bromide (20 g.) in ether (100 c.c.) was then introduced. The mixture was agitated for 12 hours and 7% potassium hydroxide solution (20 c.c.) and a further quantity of bromide (10.5 g.) were then added. After 16 hours, the faintly alkaline reaction mixture was acidified with acetic acid and the glucoside and unchanged alizarin were precipitated by addition of water (200 c.c.). A suspension of the solid in acetic acid (200 c.c.) was refluxed for 5 minutes, cooled, and filtered to remove alizarin. Addition of warm water (1 l. at 65°) to the filtrate precipitated the glucoside, con-

taminated with traces of alizarin. Recrystallisation from alcohol finally gave slender yellow needles, m. p. 206—207° after sintering at 204° (Found : C, 58.8; H, 4.9. Calc. for  $C_{28}H_{26}O_{13}$ : C, 58.9; H, 4.6%). Acetylation with acetic anhydride and pyridine during  $\frac{1}{4}$  hour on the steam-bath yielded the penta-acetyl derivative, which separated from warm alcohol in pale yellow needles, m. p. 196—197° (Glaser and Kahler, *loc. cit.*, gave m. p. 192—193°) (Found : C, 59.1; H, 4.9. Calc. for  $C_{30}H_{28}O_{14}$ : C, 58.8; H, 4.6%).

*2-β-Glucosidoxy-1-hydroxyanthraquinone.*—(A) Deacetylation was effected by the addition of 5% aqueous sodium hydroxide (30 c.c.) to a suspension of the tetra-acetyl glucoside (1.1 g.) in warm methyl alcohol (80 c.c.). The solid rapidly dissolved and the cherry-red solution, maintained at 65° for 10 minutes, deposited the sodium salt of the glucoside in dark red needles. A warm aqueous solution of this salt was acidified with acetic acid and the yellow crystalline solid was collected, washed with water, and dissolved in boiling methyl alcohol (500 c.c.). After removal of the greater part of the alcohol by distillation the glucoside crystallised; repetition of this procedure with ethyl alcohol gave alizarin glucoside in rosettes of slender yellow needles, m. p. 237° (Found : C, 59.2; H, 4.5. Calc. for  $C_{20}H_{18}O_9$ : C, 59.7; H, 4.5%) (compare Zemplén and Müller, *loc. cit.*). Acetylation with acetic anhydride and pyridine on the water-bath gave the penta-acetyl derivative, m. p. 196—197°.

(B) Treatment of the tetra-acetyl glucoside (1.1 g.) with methyl-alcoholic ammonia at 0° for 24 hours gave a dark red solid (0.8 g.) (compare Glaser and Kahler, *loc. cit.*; Zemplén and Müller, *loc. cit.*) which crystallised from a large volume of ethyl alcohol in needles, m. p. 195—196° (decomp.) (Found : C, 53.8; H, 5.3; N, 3.9%). The red solution of this compound (0.2 g.) in hot 10% acetic acid (25 c.c.) was refluxed for 6 minutes. The colour gradually changed to orange-yellow, and alizarin glucoside separated from the cooled solution, m. p. 237° after purification (penta-acetyl derivative, m. p. 196—197°). The red compound dissolved in cold concentrated hydrochloric acid to a yellow solution, and after 5 minutes addition of water precipitated alizarin glucoside, m. p. 237° after purification.

This glucoside is hydrolysed by emulsin and by warm 10% hydrochloric acid to glucose and alizarin. The cherry-red solution of the glucoside in 10% aqueous sodium hydroxide becomes violet on boiling; acidification of the cooled solution gives a precipitate of alizarin.

*2-O-Tetra-acetyl-β-glucosidoxy-1-methoxyanthraquinone.*—A mixture of the tetra-acetyl glucoside (1.2 g.), methyl iodide (3 c.c.), active silver oxide (3 g.), and acetone (30 c.c.) was refluxed for 2 hours; a test with cold alcoholic alkali then showed that methylation

was complete. After separation from the silver salts (wash with acetone), the solvent was removed under diminished pressure. The residual *methyl* ether crystallised from methyl alcohol in elongated, pale yellow prisms, m. p. 155—156°,  $[\alpha]_D^{17} -71.72^\circ$  in acetone (Found: C, 59.1; H, 5.1.  $C_{29}H_{28}O_{14}$  requires C, 59.5; H, 4.8%). It is readily soluble in warm alcohol or acetone, and does not give a coloration with cold alcoholic sodium hydroxide. A solution of the ether (1.2 g.) in a mixture of methyl alcohol (30 c.c.) and concentrated hydrochloric acid (15 c.c.) was refluxed for 2 hours. Addition of water (50 c.c.) to the cooled solution precipitated 1-methyl alizarin, which crystallised from methyl alcohol in orange-yellow needles, m. p. 179°. Acetylation of the latter substance with acetic anhydride and sodium acetate gave 1-methyl-2-acetyl alizarin, yellow needles from methyl alcohol, m. p. 212° (Found: C, 69.1; H, 4.4. Calc. for  $C_{12}H_{12}O_5$ : C, 68.9; H, 4.1%).

*2-3-Glucosidoxy-1-methoxyanthraquinone*.—10% Methyl-alcoholic sodium hydroxide (15 c.c.) was added to a warm solution of the tetra-acetyl derivative (1 g.) in methyl alcohol (30 c.c.). The mixture became red owing to slight decomposition of the glucoside, and after 2 hours at room temperature 10% acetic acid (10 c.c.) was added. On evaporation of the methyl alcohol in a vacuum the *glucoside* gradually separated. After being kept for 12 hours in an ice-chest, the solid was separated from the faintly alkaline mother-liquor and washed with alcohol to remove traces of alkali. On crystallisation from methyl alcohol it formed clusters of slender yellow needles, m. p. 230—231° (Found: C, 60.2; H, 5.0.  $C_{21}H_{20}O_9$  requires C, 60.6; H, 4.8%). The glucoside is sparingly soluble in cold alcohol, water, or acetone, and does not give a coloration with cold alcoholic sodium hydroxide. It is readily hydrolysed by emulsin to 1-methyl alizarin and glucose.

*Alizarin Octa-acetyl Maltoside*.—*O*-Hepta-acetylmaltosidyl bromide was prepared by the following method (compare Zemplén, *Ber.*, 1928, **61**, 927). Acetic anhydride (25 c.c.) was added to a solution of octa-acetyl maltose, m. p. 160° (50 g.) in acetic acid saturated at 0° with hydrogen bromide (100 g.). After 5 hours at room temperature the reaction mixture was diluted with chloroform (400 c.c.) and poured on ice (300 g.) in water (300 g.). The chloroform layer was separated, washed three times with ice-water (300 c.c.), and dried over calcium chloride. On removal of the solvent in a vacuum the bromide remained as a pale straw-coloured syrup (40 g.), which solidified on trituration with ligroin.

A solution of amorphous *O*-hepta-acetylmaltosidyl bromide (20 g.) in ether (150 c.c.) was added to a mixture of alizarin (8 g.), potassium hydroxide (1.2 g.), and 50% aqueous acetone (200 c.c.).

After agitation for 24 hours the faintly alkaline mixture was acidified with acetic acid, and the precipitate of alizarin removed by filtration. The ethereal layer was separated, and the aqueous solution extracted once with ether (100 c.c.). An acetic acid solution of the residue obtained on evaporation of the ether was kept in the ice-chest for 24 hours, filtered to remove alizarin which had crystallised, and then poured into water (500 c.c. at 50°). The orange solid which separated was immediately collected, washed with water, and dissolved in hot alcohol. On cooling, an amorphous, bright yellow solid separated. Purification by hot alcohol was repeated (five times) until a specimen gave a bright cherry-red colour in cold alcoholic sodium hydroxide. Acetylation of the purified amorphous solid with acetic anhydride and sodium acetate on the steam-bath during 6 hours gave *alizarin octa-acetyl maltoside*, which crystallised from alcohol in pale yellow needles (1.6 g.), m. p. 185°,  $[\alpha]_D^{25} -20.05^\circ$  in acetone (Found: C, 55.8; H, 5.1.  $C_{42}H_{44}O_{22}$  requires C, 56.0; H, 4.9%). The substance is readily soluble in warm alcohol or acetone and in cold acetic acid.

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## CXLV.—*The Octammines, with Special Reference to Tin.*

By ARTHUR JAMES COOPER and WILLIAM WARDLAW.

So far, no octammine has been prepared by a reaction between a metallic salt and ammonia in the presence of water, whereas under similar experimental conditions very stable hexammines have been isolated. This supports Sidgwick's view ("The Electronic Theory of Valency," p. 156) that covalencies of eight only arise, even with atoms capable of exhibiting them, in exceptionally favourable circumstances.

Nevertheless, by the action of liquid or gaseous ammonia on metallic salts or their solutions in non-aqueous solvents, a number of compounds containing eight molecules of ammonia have been described, and in many text-books they are formulated and considered as typical co-ordination compounds. This formulation, in the case of unstable substances such as  $[Ti, 8NH_3]Cl_4$  and  $[Ca, 8NH_3]Cl_2$ , is difficult to justify, for it implies a covalency of eight for the metallic

atoms when the weight of chemical evidence is against such an assumption. Even with  $\text{BaBr}_2 \cdot 8\text{NH}_3$ , it is questionable whether the formula  $[\text{Ba} \cdot 8\text{NH}_3] \text{Br}_2$  is satisfactory, for it is recorded (Joannis, *Compt. rend.*, 1891, **112**, 339) that on exposure to the air the ammonia is completely liberated. It is possible that here, as in the cases cited above, the molecules of ammonia are polymerised or that some form part of the crystal unit but not of the complex molecule.

The zirconium salt  $[\text{Zr} \cdot 8\text{NH}_3] \text{Cl}_4$ , prepared by Stähler and Denk (*Ber.*, 1905, **38**, 2611) by the passage of ammonia into an ethereal suspension of zirconium chloride, is sufficiently stable to yield correct analytical figures, and therefore may be considered a true co-ordination compound; nevertheless, it readily loses ammonia and is affected by moist air. Octammines of cerium, samarium, and neodymium are stated to be formed as intermediate products in the degradation of compounds of higher ammonia content, but here again the evidence in favour of the formation of a true co-ordination compound is very slight. An octammine of thorium is supposed to exist (Ephraim, "Inorganic Chemistry," p. 280), but the experimental evidence (Chauvenet, *Compt. rend.*, 1910, **151**, 387) is not conclusive for such an assumption.

The remaining case of a supposed octammine is the compound  $[\text{Sn} \cdot 8\text{NH}_3] \text{I}_4$ . It was prepared as a white substance by Ephraim and Schmidt (*Ber.*, 1909, **42**, 3856) on passing ammonia into a solution of stannic iodide in carbon disulphide, the solvent then being evaporated by means of warm water. Their product gave Sn, 15.74;  $\text{NH}_3$ , 16.47 (Calc. for  $\text{SnI}_4 \cdot 8\text{NH}_3$ : Sn, 15.61;  $\text{NH}_3$ , 17.84%). By direct combination of ammonia and stannic iodide in the absence of a solvent, a compound was obtained giving Sn, 15.71, 15.57, 15.01;  $\text{NH}_3$ , 16.91, 16.90%. The formation of the co-ordination compound is inferred, therefore, rather than proved by the experimental results.

As stannic iodide is soluble in other organic solvents, it seemed of interest to reinvestigate the reaction in another medium, as well as to repeat the work of Ephraim and Schmidt with carbon disulphide as a solvent. In no case was an octammine formed of sufficient stability for it to be isolated and analysed as such. It appears, therefore, that only in the case of the zirconium salt,  $\text{ZrCl}_4 \cdot 8\text{NH}_3$ , is there any experimental evidence for the existence of a co-ordination compound of the type  $[\text{R} \cdot 8\text{NH}_3] \text{X}_4$ .

We found, however, that in every case the compound could not consist exclusively of tin, halogen, and ammonia: the analytical figures indicated the necessity for a fourth constituent of the molecule. Water was obviously the only possible addendum, and this view was confirmed by the fact that the hydrogen content of the

compound was in excess of that required by the nitrogen present. Undoubtedly, therefore, the products were of the type  $[\text{Sn}, x\text{NH}_3, y\text{H}_2\text{O}]\text{I}_4$ , and it was found on calculating the value of the different units that  $x + y$  was approximately equal to 8. Thus, although the actual octammine was not capable of isolation under the experimental conditions outlined above, yet there is evidence that such an unstable octammine can exist but that the molecules of ammonia are rapidly replaced in the air by water molecules.

A study has also been made of the reaction between stannic iodide in carbon tetrachloride and organic bases such as aniline, pyridine, and quinoline. In no case was there co-ordination of eight molecules of these substances. It appeared that the stable products obtained were of the type  $\text{SnI}_4 \cdot 2 \cdot 5\text{R}$  ( $\text{R} = \text{aniline or pyridine}$ ).

Scagliarini (*Atti R. Accad. Lincei*, 1925, **1**, 582) records the isolation of  $\text{SnI}_4 \cdot 5\text{C}_6\text{H}_{12}\text{N}_4$  from the reaction of hexamethylene-tetramine with stannic iodide in chloroform solution, and also a deep violet substance of the type  $\text{SnI}_4 \cdot 4\text{C}_6\text{H}_{12}\text{N}_4 \cdot 2\text{CHCl}_3$ , which undergoes little change at  $80^\circ$  or in a vacuum over sulphuric acid but is rapidly decolorised by moist air. Here, if one considers that the non-polar stannic iodide becomes a polar compound after the reaction, a maximum co-ordination number of *six* is attained in the last compound.

#### EXPERIMENTAL.

The experiment of Ephraim and Schmidt (*loc. cit.*) was repeated, gaseous ammonia being passed through stannic iodide dissolved in carbon disulphide, which at the same time was slowly evaporated. The white product was unstable, continually evolving ammonia, and after a state of stability appeared to have been attained, its *maximum* ammonia content was 13.3%, Sn being 15.3% ( $\text{NH}_3 : \text{Sn} = 6.07 : 1$ ). It was noted that a red intermediate compound was formed during the passage of the ammonia through the solution.

A new series of experiments was instituted in which carbon tetrachloride was used as the solvent instead of carbon disulphide. The stannic iodide was dried in a vacuum over phosphoric oxide, and the tetrachloride kept for several days over phosphoric oxide and then distilled from fresh phosphoric oxide. The ammonia was carefully dried by passage over lime and solid caustic potash. The same red intermediate product referred to above resulted and gradually turned white. The tetrachloride could not conveniently be removed by simultaneous evaporation, as in the case of carbon disulphide, so the product was obtained by filtration. An immediate analysis gave Sn, 15.74;  $\text{NH}_3$ , 12.7%. In other experiments, similarly conducted, the figure for ammonia was never exceeded. After the substance had

been kept for several days in a desiccator over calcium chloride, the ammonia content fell to 9.38% and the tin to 15.4%.

The red intermediate compound when dried yielded a dull brown substance which was quite stable in air and gave Sn, 16.23;  $\text{NH}_3$ , 6.63. Since  $\text{SnI}_4 \cdot 3\text{NH}_3$  requires Sn, 17.53;  $\text{NH}_3$ , 7.53, it was evident that the red compound had absorbed moisture from the air in place of liberated ammonia. This view was confirmed by microanalysis of a sample of a white compound which yielded Sn, 15.52; N, 6.8; H, 2.8. Such a substance corresponds to the composition Sn, 15.52; I, 66.4;  $\text{NH}_3$ , 8.25;  $\text{H}_2\text{O}$ , 10.05% ( $\text{Sn} : \text{I} : \text{NH}_3 : \text{H}_2\text{O} = 1 : 4.00 : 3.71 : 4.27$ ; i.e.,  $\text{Sn} : \text{NH}_3 + \text{H}_2\text{O} = 1 : 7.98$ ). Hence the compound can be considered as  $\text{Sn}[x\text{NH}_3 + (8 - x)\text{H}_2\text{O}]\text{I}_4$ , with a co-ordination number of eight. Moreover, a similar expression can be deduced for the composition of each of the white compounds described above.

The white compounds are generally unstable, and dissolve easily in the cold in dilute hydrochloric or nitric acid to a colourless solution. With more concentrated nitric acid they give a copious yield of iodine.

*Stannic Iodide and Pyridine.*—The attempt to prepare a pyridine compound by acting on stannic iodide in carbon tetrachloride proved abortive; the dark red product proved to be stannic iodide. Other solvents were tried, and finally benzene dried by two distillations over phosphoric oxide was chosen. The pyridine was dried by standing for a week over solid caustic potash, followed by two distillations from barium oxide. When the pyridine was added to a benzene solution of stannic iodide, a brown stable precipitate resulted which was insoluble in dry alcohol. It was washed with benzene and with dry alcohol and dried in a desiccator over calcium chloride. The substance was crystalline, and soluble in dilute hydrochloric and sulphuric acids. It was partly soluble in water and underwent hydrolysis on standing. With dilute nitric acid, iodine was liberated.

*Analysis.* The tin was estimated by repeated evaporation with dilute nitric acid and twice with concentrated acid. The residue was ignited slowly at first and afterwards over the blowpipe till of constant weight (Found: Sn, 14.4; I, 61.4; N, 4.37.  $\text{SnI}_4 \cdot 2.5\text{C}_5\text{H}_5\text{N}$  requires Sn, 14.3; I, 61.7; N, 4.25%).

*Stannic Iodide and Aniline.*—Considerable difficulty was found in preparing this compound. A red crystalline substance formed on addition of dry aniline to a solution of the iodide in dry carbon tetrachloride, but immediately on exposure to the air the colour changed to a light fawn. This could not be due to loss of aniline and was attributed to hydrolysis. To obviate exposure to the air, the



preparation flask was attached by means of a wide V-shaped tube, in which the apex was replaced by a ground joint, to a sintered-glass funnel fitted with a rubber stopper. On rotating the flask about the joint, the mixture it contained was transferred to the sintered-glass funnel without exposure to air. Carbon tetrachloride was introduced into the flask through a second side-tube in the cork, and the product washed repeatedly on the funnel. It was then quickly dried on filter paper and transferred to a vacuum desiccator. A rich-brown *substance* resulted which was quite stable. It dissolved in dilute nitric acid on warming, but on boiling, iodine was copiously evolved. It readily dissolved in dilute hydrochloric or sulphuric acid to a yellow solution. It was rapidly hydrolysed by dilute acetic acid.

*Analysis.* Treatment with dilute nitric acid and evaporation was unsatisfactory, for the presence of the aniline produced a somewhat violent reaction on concentration, and the base could not be quantitatively expelled. Finally, the compound was decomposed by treating it with ammonia ( $d\ 0.880$ ), and evaporating the mixture first to dryness on the water-bath, and then several times with water to expel the aniline which had been set free. The residue was treated with concentrated nitric acid, evaporated to dryness on the water-bath, gently heated for some time in an air-bath, and finally heated till of constant weight over the blowpipe (Found: Sn, 13.0; N, 3.76; Sn : N = 1 : 2.45.  $\text{SnI}_4 \cdot 2.5\text{C}_6\text{H}_5 \cdot \text{NH}_2$  requires Sn, 13.7; N, 4.0.  $\text{SnI}_4 \cdot 2\text{C}_6\text{H}_5 \cdot \text{NH}_2$  requires Sn, 14.6; N, 4.35%).

*Stannic Iodide and Quinoline.*—On addition of quinoline to a solution of stannic iodide in carbon tetrachloride, a black solid resulted which, on removal from the solvent, rapidly turned stone-coloured, owing probably to hydrolysis. A stable product was obtained, however, by refluxing the mixture for 2 hours. The product was washed with carbon tetrachloride and dried in a vacuum desiccator for 2 days. It remained unaltered in colour, was sparingly soluble in water, and soluble in dilute hydrochloric or sulphuric acid, whilst dilute nitric acid liberated iodine. Nevertheless, analysis (Found: Sn, 12.8; I, 51.9.  $\text{SnI}_4 \cdot 2.5\text{C}_9\text{H}_7\text{N}$  requires Sn, 12.45; I, 53.5%) indicates that the substance was not pure.

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CXLVI.—*On Active Nitrogen. Part VIII. (i) The Influence of Photogens and of Surfaces upon Glow Phenomena in Nitrogen. (ii) The Effects of Addition of Other Gases to Luminous Nitrogen.*

By ERIC JOHN BAXTER WILLEY.

*Section (i).*

It was shown in Part VII (this vol., p. 336) that the decay of the nitrogen after-glow is markedly controlled in its kinetic aspects by the purity of the gas employed, for a number of observations were satisfactorily explained upon the hypothesis that the action of the impurities (which, it now appears, must certainly be present to the extent of about 0.1% in order that the yellow luminescence may be exhibited) is to cover the walls of the reaction vessels, thus converting what would otherwise be a "dark" heterogeneous recombination of atoms into a homogeneous process accompanied by the emission of the after-glow. When adequate quantities of these photogens are present or pressure conditions are such that the walls may be supposed covered by nitrogen, the volume decay process is influenced by the over-all gas pressure in a manner which permits of the reaction being expressed as a third-order change, probably  $N' + N + N_2 \longrightarrow 2N_2 + \text{after-glow}$ , where  $N'$  is a metastable atom with an energy of 2.3 volts, in agreement with calculations given in the same paper.

It follows from this theory that it should be possible to enhance the luminosity of a stream of nitrogen by adding the photogen above or below the discharge, always provided, in the first case, that it be not destroyed by the spark. An attempt made by Lewis (*J. Amer. Chem. Soc.*, 1929, **51**, 654), however, in which nitrogen at a fraction of 1 mm. pressure was subjected to the electrodeless discharge and then rapidly treated with a small amount of oxygen, did not show the effect anticipated. This may have been due either to the hypothetical wall reaction being so rapid that all the atoms had recombined before the oxygen reached the surfaces, or else to too much oxygen having been added, the small glow being catalytically destroyed at once; a further possibility is that suggested by Lewis, *viz.*, that ordinary oxygen plays no part in the production of the after-glow. Experiments are now described which prove directly that the photogens act, at any rate in the case studied, after the nitrogen has been through the discharge, and that their effects can be reproduced by changing the walls of the vessel, probably the most weighty evidence yet presented in favour of the hypothesis that photogens are essentially wall-poisons.

## EXPERIMENTAL.

The observation tube employed in these experiments was  $80 \times 3$  cm., and arrangements were made for the admission to it of (a) nitrogen (purified by hot copper, etc., as described in Part VII, *loc. cit.*), and (b) hydrogen similarly treated; both of these gases could be passed through powerful discharges (condensed or not, as desired), which were operated independently from different electrical circuits. The down-stream end of the tube was closed by means of a rubber bung, faced on the inside with a polished aluminium disc, which was cut to fit the glass tube accurately and held in position by a rod passing through the bung and rendered vacuum-tight by picein wax applied to the outside; the exhaust line was taken off some 20 cm. above this end, and the space between the side tube and the bung disc was filled with tightly packed tin-foil to prevent access of the active nitrogen to any rubber surfaces accidentally exposed. After leaving the discharge, the two gases flowed through some 20 cm. of 5 mm.-bore tubing bent in a W-shape and blackened to prevent light from the discharges reaching the observation tube, the inlet for the hydrogen being about 10 cm. below that for the nitrogen; traps cooled by liquid air were placed in the exhaust line for the collection of products of any reaction between active nitrogen and active hydrogen, it having been stated that under these conditions ammonia is formed (Lewis, *J. Amer. Chem. Soc.*, 1928, 50, 27). The glow was measured by means of the caesium photocells employed in the earlier investigation (Part VII).

*Addition of Photogens below the Discharge.*—Nitrogen (prepared as described in Part VII, and containing 0.3% of argon and less than 0.01% of other gases) was allowed to stream through the apparatus for 3 hours at the rate of 2500 c.c./hour, the discharge being maintained as usual and the pressure kept at 4 mm. of mercury. The after-glow rapidly became faint in the observation tube, and when at the end of this period it had practically vanished, a small current of hydrogen (300 c.c./hour) was fed through the second inlet to the tube. No effect upon the glow was observed as long as the hydrogen was inert, but when the hydrogen discharge was switched on, the yellow nitrogen after-glow appeared with great brilliance, only to disappear in a few seconds when the second (hydrogen) discharge was interrupted.

A second experiment was then performed in which 0.06% of a 1:1 nitrogen-oxygen mixture was fed to the nitrogen above its discharge. The glow was thus developed sufficiently to permit of its being measured, and the corresponding decay curve was of the same form as Curve A, Fig. 1 of Part VII (*i.e.*, steep and strongly

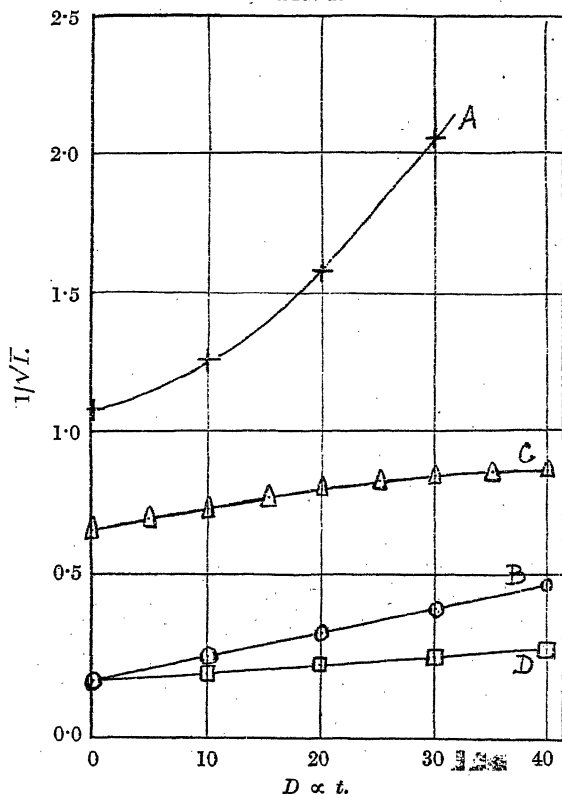
curved); the feed of hydrogen was as before, and the brightening of the glow again appeared when the second discharge was started, the decay curve then showing a closely linear relation between  $1/\sqrt{I}$  and time ( $I$  = glow intensity, here proportional to photo-electric current) exactly as in the figure mentioned. Since, when the hydrogen was sparked alone, the feed of nitrogen being shut off, ammonia condensed in the traps cooled by liquid air in the exhaust line, the hydrogen was analysed; it was found to contain 0.04% of nitrogen, derived from the water in the Boyle-bubbler aspirator in which the hydrogen had been stored. When the air in the constant-pressure reservoir of this device was replaced by hydrogen, tests for nitrogen in the gas stored under the new conditions were negative; and at the same time the pure hydrogen lost its ability to enhance the nitrogen after-glow when sparked, as in the experiments just described. For later experiments, a trap filled with activated charcoal and cooled by liquid air was added to the hydrogen circuit, and this satisfactorily removed the traces of nitrogen. It appeared, then, that a small amount of nitrogen is an essential ingredient of the hydrogen if, upon sparking, this gas is to enhance the glow in fairly pure nitrogen, a supposition verified by experiment.

The explanation of the phenomenon is clear: the discharge in hydrogen containing a trace of nitrogen produces a small amount of ammonia, and this, when added to the nitrogen below the discharge, produces an effect which is simulated exactly by the admission of other photogens above the discharge. It was therefore anticipated that addition of hydrogen to nitrogen above the discharge would lead to a strong glow, and this was in fact observed, provided that a feed of some 1% was employed in order that the nitrogen-hydrogen-ammonia equilibrium should not yield a merely insignificant proportion of the last substance. It may be mentioned that, with the small feed of pure and sparked hydrogen to the glowless nitrogen, mentioned earlier, no ammonia could be detected save after very long runs. With photogenic nitrogen and larger feeds of hydrogen, the yellow after-glow was markedly reduced when the latter gas was sparked, and at the same time small amounts of ammonia condensed in the traps, in agreement with Lewis's observations (*loc. cit.*). It must, however, be emphasised that the hydrogen must be in large excess, otherwise no ammonia is obtained. This matter is now being investigated quantitatively, and it appears that there are probably several factors operating simultaneously which render the case rather complicated.

*The Influence of Surfaces upon the Decay of the After-glow.*—(a) According to the views expressed earlier, *viz.*, that photogens are

wall-poisons and inhibit the non-luminous heterogeneous reassociation of atoms, thus favouring the volume process which gives rise to the after-glow, it follows that a glow should be induced in pure, non-photogenic nitrogen which, at the time of sparking or immediately afterwards, is placed in contact with the right kind of surface.

FIG. 1.



Curve A: "pure" nitrogen, glass surface.

Curve B: photogenic nitrogen, glass surface.

Curve C: "pure" nitrogen, paraffined surface.

Curve D: photogenic nitrogen, paraffined surface.

It would also be expected that the glow decay process in pure nitrogen should pass to that observed in the photogenic gas if the reaction could be studied in vessels with adequately poisoned walls.

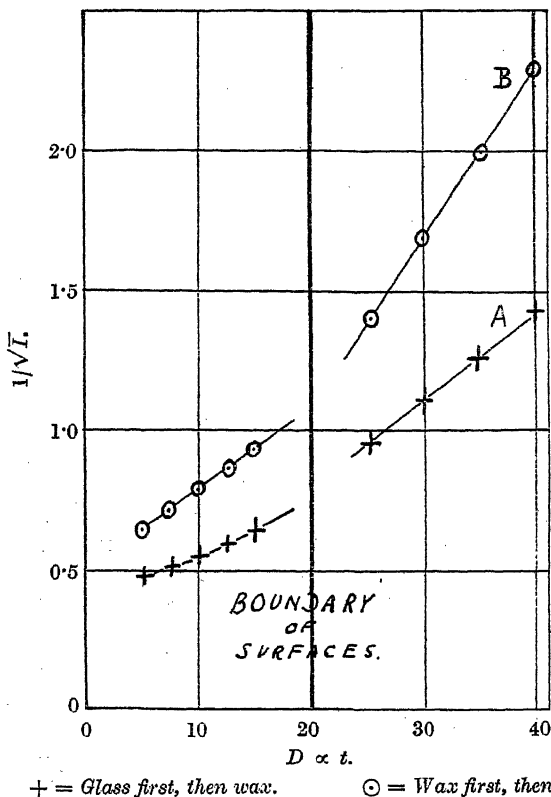
A simple modification of the apparatus just described enabled this to be done. Tubes were cut from wide-bore glass tubing, of external diameter such that it just fitted into the main observation tube, and coated on the inside with various waxes and transparent

varnishes, thus enabling the glow decay to be studied as the stream passed over the different treated surfaces. Many organic substances were tried, but in every case save one the glow became blue and hydrogen cyanide condensed in the traps, so that the chemical action rendered true decay studies out of the question. A high-melting wax of the type employed in electrical work was eventually found which reacted a little at first, but upon prolonged exposure to the active nitrogen stream gave hydrogen cyanide in amounts which could be detected only by the guaiacum-copper sulphate method (Anderson, *Z. anal. Chem.*, 1916, **55**, 459) and corresponded to a concentration of less than 0.0003% of the latter gas in the nitrogen. A series of decay runs was then made and the results are shown in Fig. 1.

Curves A and B exhibit the marked difference in form and slope of the  $1/\sqrt{I}-t$  graphs found in the experiments discussed in Part VII for "pure" and photogenic nitrogen, Curve A being of the form which we have ascribed to the superposition of a strong wall decay upon the volume reaction, and Curve B being that corresponding with the bimolecular and homogeneous process; for both of these runs a clean glass tube was fitted in the main observation tube. The results shown in Curves C and D relate to precisely similar experiments wherein the clean glass tube was replaced by one coated on the inside with a thin uniform layer of the wax mentioned above; the decay in the photogenic nitrogen (Curve D) is even less than in the case of Curve B, but Curve C shows that the expected development of a strong glow in pure nitrogen and the retardation of its decay by the influence of highly poisoned walls are actually realised. It is, moreover, noticeable that up to the 15 cm. point, the curve is almost parallel to Curve B (photogenic nitrogen and a clean glass surface), but that subsequently the slope falls off. That this was not due to inequalities in the wax coating, leading to variations in the amount of light transmitted, was proved by reversing the tube, whereupon the effect was seen just as before; further, the galvanometer deflexions were so large that any error in reading must also be ruled out as an explanation of this curious effect. The author suggests that it is due to the formation of a trace of hydrogen cyanide in the first few cm. of the waxed tube; this gas then acts as photogen and further poisons the paraffin surface, since the effect is not seen in Curve D where larger concentrations of photogen are present. Even if one ignores the possible influence of very small quantities of hydrogen cyanide, it is clear that the paraffined surface is able *per se* to reproduce the effects associated with photogens, thus affording strong confirmatory evidence as to the probable truth of the wall-poison theory.

It followed from the observations described above that it should be possible to vary the decay rate of a stream of glowing nitrogen by drawing it first over clean glass and then over an inactive surface of the type just employed. The waxed tube used earlier was therefore cut in two, one half was carefully cleaned, and further decay runs were made in which glow streams obtained from gases containing 0.03% and *ca.* 0.15% of oxygen as photogen were drawn first over

FIG. 2.



the clean and then over the paraffined glass, the tubes being slipped into the main observation tube to occupy the same position as that taken by the single tube from which they were made. With 0.03% of photogen present, the graph of  $1/\sqrt{I}$  against the distance along the tube (proportional to time) was markedly curved for the glass surface (Fig. 2, Curve A), but linear for the paraffin; increase of the quantity of photogen to 0.15% gave a plot which was linear and showed no discontinuity, as in the former case, at the

junction of the two surfaces. The tubes were then reversed so that the glow came into contact first with the paraffin and then with the glass, and a decay run here revealed that, although with 0.15% photogen the  $1/\sqrt{I-t}$  plot was linear over the entire length of both tubes as in the corresponding experiment just given, yet with the 0.03% photogen content the break again occurred at the junction of the two surfaces (Fig. 2, Curve B), and that the graph was linear for both the paraffin and the glass but steeper in the latter case. The linearity for the glass may here be due to a trace of hydrogen cyanide being produced when the active nitrogen is in contact with the wax, this gas acting to a certain extent as a photogen and repressing the wall reaction. This shows that with a high photogen concentration the decay rate is, so far as paraffin and glass are concerned, independent of the nature of the surfaces, but with purer nitrogen the decay is very susceptible to wall influence.

A final and conclusive piece of evidence upon this point was provided by the observation that the amounts of hydrogen cyanide formed in the experiments by interaction of the active nitrogen and the paraffin were much less when the photogenic gas was employed than with the purer material; this clearly suggests that the photogens cover the paraffin with a film protective against the active nitrogen.

#### *Section (ii).*

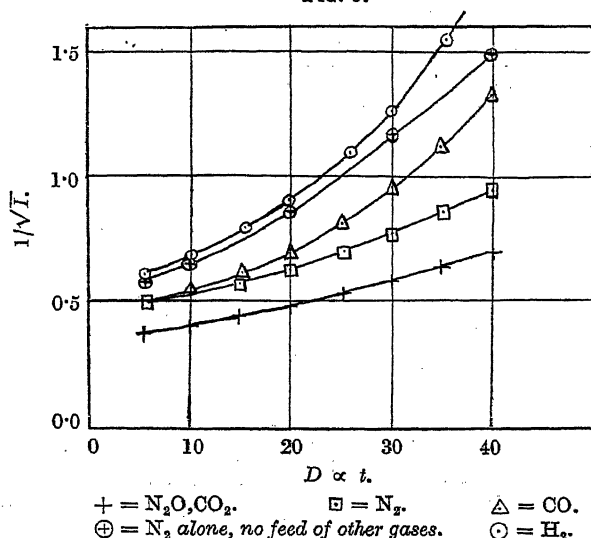
The theory that the after-glow results from a ternary reaction,  $2N + N_2 \longrightarrow 2N_2 + \text{after-glow}$ , was advanced about the same time by Fri. Sponer (*Z. Physik*, 1925, **34**, 622) and by Willey and Rideal (Part I, J., 1926, 1804). The first author based her opinion upon spectroscopic observations, considered in conjunction with the old idea of Clausius, revived by Herzfeld (*Z. Physik*, 1922, **8**, 132), Born and Franck (*Ann. Physik*, 1925, **76**, 225), and others, as to the necessity for the presence of an acceptor for the energy of association of atoms in order that a stable molecule might be formed. On the other hand, Willey and Rideal were influenced by the long life of the glow-emission reaction, comparable in speed with the slow ternary process  $2NO + O_2 \longrightarrow 2NO_2$ , and by the negative temperature coefficient of the glow decay, another feature of the termolecular change just quoted. In both cases the rôle of the third entity was considered specific, and the possibility was not envisaged of the molecule of nitrogen being replaced by one of another element without affecting the glow, although it was admitted that in some examples (but not the majority) of the excitation of metallic spectra by active nitrogen, a metal atom might act as the entity concerned (Part IV, J., 1927, 2831).

According to this theory, therefore, the initial intensity of the



after-glow should be increased at the expense of its duration if nitrogen is added; the luminosity per unit volume of nitrogen should be unaffected, however, if the diluent gas is of another kind and is such as not to react chemically with the active nitrogen or, by reason of its excitation potentials, is not likely to be able to accept energy from the molecule emitting the after-glow radiation, and thus interfere with the normal glow decay process (compare Part II, J., 1927, 669). As mentioned in Part VII (*loc. cit.*, p. 343), there is divergence of experimental evidence upon this point,

FIG. 3.



Kneser having obtained a positive result which Bonhoeffer and Kaminsky had been unable to observe earlier. Kneser has extended the original hypothesis in view of his finding that the addition of argon produces the same effect as nitrogen, and according to his work the third substance need not necessarily be nitrogen; the present author has also described experiments (Part VII) which show that the walls of the apparatus may under appropriate conditions act in the same way. An experimental study of the addition of other gases to the glow has therefore been made, and the conclusion is reached that the ternary reaction with nitrogen as the specific third entity is most probably responsible for the glow emission.

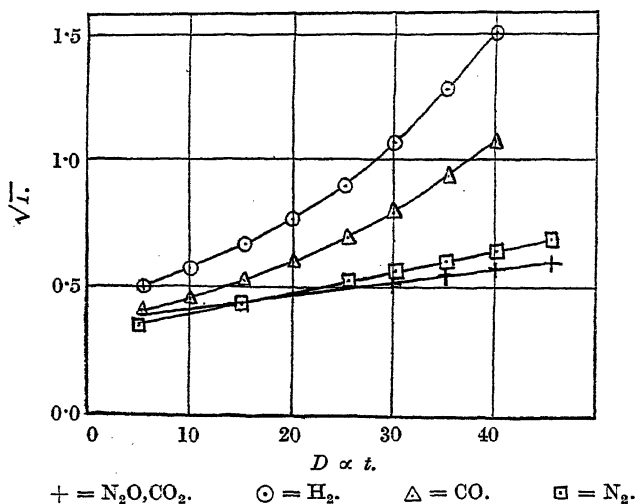
#### EXPERIMENTAL.

The gases were admitted from a calibrated gas burette and capillary backed by a fine adjustment tap, and entered the glow

stream at the inlet B (see Part VII, p. 337), *i.e.*, below the discharge, and the quantity added was, in all cases, 15% of the flow of nitrogen, *i.e.*, 300 c.c. of diluent to 1950 c.c. of nitrogen per hour; the glow decay was, as usual, measured with the caesium photocells. The results are illustrated in Figs. 3 and 4.

In Fig. 3 are shown the curves obtained with equal feeds of carefully purified hydrogen, carbon monoxide, nitrous oxide, carbon dioxide, and nitrogen, and in Fig. 4 are given corresponding results obtained by using the nitrogen containing *ca.* 0.07% of oxygen as photogen. It will be seen that with feeds of nitrous oxide and carbon dioxide, the decay curves are practically coincident and

FIG. 4.



linear for both photogenic and "pure" nitrogen, but with carbon monoxide and hydrogen the curves are much flatter when 0.07% oxygen is present in the nitrogen than when only 0.03% is there. Moreover, with the first two gases the glow is brightened during the whole of its passage down the observation tube. The results agree in a striking manner with both the three-body collision theory and the view advanced as to photogens being wall-poisons.

Let us first consider the results with the "pure" nitrogen, temporarily ignoring the results obtained with the inert nitrogen as diluent. It has already been shown that the introduction of a photogen *below* the discharge enhances the glow, and as photogens are almost certainly gases which are strongly adsorbed by glass, we should expect, making the usual assumption that at these pressures the adsorption of a gas varies inversely as its boiling point, that

easily condensable gases (*e.g.*, nitrous oxide, carbon dioxide) would reduce wall activity and thus intensify the glow more than those difficult to liquefy (*e.g.*, carbon monoxide, nitrogen); this is actually observed (Fig. 3), the decay curves with feeds of the two last-named gases being of the type associated with "pure" nitrogen (compare Curves A and B, Fig. 1, Part VII), while with the other pair the plot is typically that of a glow stream produced in highly photogenic nitrogen, and, most of all, the retardation of the rate of decay is in exactly the inverse order of the boiling points of the gases concerned (hydrogen, b. p.  $-253^{\circ}$ ; nitrogen,  $-196^{\circ}$ ; carbon monoxide,  $-191^{\circ}$ ; nitrous oxide,  $-90^{\circ}$ ; carbon dioxide,  $-78^{\circ}$ ).

With photogenic nitrogen (0.07% oxygen) the walls are fairly well covered, and hence the decay with feeds of carbon monoxide and nitrogen approximates to that observed in the less pure nitrogen alone, while with feeds of carbon dioxide and nitrous oxide the adsorption is complete. It would thus be expected that with a glow stream of high photogen concentration the decay curves obtained with feeds of all these four gases should be linear and coincident, and this has actually been found for nitrogen containing 0.12% of oxygen.

The case where the gas added is nitrogen is more complicated, for two factors have to be considered, *viz.*, (i) the adsorption or photogen effect, and (ii) the direct participation by the added nitrogen in the homogeneous glow-emission process, in accordance with the specific three-body collision theory. These two factors are considered separately. (i) It has already been shown (Part VII) that the wall effect is probably much reduced at higher over-all pressures of nitrogen, and we should therefore expect that the addition of nitrogen would reduce the rate of decay of the glow in the moderately pure gas, and, by diminishing the surface reactions, automatically lead to a straightening of the  $1/\sqrt{I-t}$  graph, which should (in this consideration alone) lie between the curves for hydrogen and carbon monoxide; in photogenic nitrogen, however, nitrogen should have no more effect than any of the other gases when added to the glow stream. (ii) It being assumed that the glow emission results either from a triple impact  $N + N' + N_2 \longrightarrow 2N_2 + \text{after-glow}$ , or a reaction  $N + N' \longrightarrow N_2'$ , followed rapidly by  $N_2' + N_2 \longrightarrow 2N_2 + \text{after-glow}$ ,  $N'$  being a metastable 2.3-volt atom and  $N_2'$  an excited or metastable molecule (11 volts), it follows that the initial intensity of the glow should be increased and its duration diminished by addition of nitrogen. We might thus expect that with the combined operation of both these factors, the decay should correspond with that observed in nitrogen at a fairly high over-all pressure, *i.e.*, would give a linear  $1/\sqrt{I-t}$  plot

of fairly steep slope, whereas Fig. 3 shows that the graph is slightly curved and nearly parallel to that for the experiments wherein the gases added were nitrous oxide and carbon dioxide; apparently, then, in this case the greater part of the influence of the added nitrogen goes to suppress the wall reaction.

In Fig. 4 a different state of affairs is revealed, the surfaces being to a large extent "poisoned"; the action of the added nitrogen is then apparent in the gas phase, for the  $1/\sqrt{I}-t$  plot, although linear, is rather steeper than that for the runs where the diluent gases were carbon dioxide and nitrous oxide, i.e., the initial glow intensity and its rate of decay are increased and the duration of the luminosity is diminished by the addition of nitrogen, as demanded by the ternary reaction theory.

A second set of experiments, in which the feeds of gas added were increased to 30%, gave the same types of decay curve, with the exception that, as would be expected, the positive result of the triple-collision theory test by addition of nitrogen, as in the experiments illustrated in Fig. 4, was more marked than when only 15% of diluent was employed.

#### Discussion.

The experiments upon the influence of a waxed surface upon glow phenomena described in the first part of this paper afford fairly conclusive proof of the theory that photogens are wall-poisons as suggested in Part VII, and further comment is unnecessary.

The observations upon the addition of other gases to the after-glow may be considered in conjunction with the work of Constantinides (*Physical Rev.*, 1927, 30, 95) and of Bonhoeffer and Kaminsky (*loc. cit.*). The former, in the course of some investigations upon ionisation in active nitrogen, studied the diminution in the life of the after-glow brought about by addition of helium, nitrogen, hydrogen, and oxygen, and found their destructiveness to increase in the order given; helium was remarkable in that it had practically no action. As no mention is made in his paper of any precautions to keep absolutely constant the composition of the nitrogen in which the glow was produced, it is doubtful whether his results can be compared with those of the author given in Part VII and in the present communication, but it is noticeable that the rate of decay increased from nitrogen to hydrogen, as in the experiments here described when the gas was not rich in photogens. Oxygen appears to participate in the glow-emission reaction because of the many levels it possesses at which it can absorb energy, and hence it should not be considered in purely kinetic studies; in the case of helium, however, it appears either that, as Constantinides points out, its

lowest excitation level (20 volts) is so high that it cannot acquire energy from the active nitrogen and hence has no effect whatever upon the glow, or that, in this particular experiment, highly photogenic nitrogen was being used and no influence upon the rate of decay was noticed, since the helium could influence neither the state of the walls nor the volume reaction, in accordance with the specific three-body collision theory.

Bonhoeffer and Kaminsky added inert nitrogen to a stream of the glowing gas, and, observing no enhancement of the glow and a diminution of its life, concluded that the decay of the after-glow is not a third-order reaction. This may have been due partly to the design of the apparatus they employed, which would lead to very gradual mixing of the added gas with the glow stream (see footnote, p. 243 of Kneser's article, "Der aktive Stickstoffe," *Ergebnisse der exakten Naturwissenschaften*, 1929, 8, 229; an admirable summary of work to date) or to their experimental conditions having been comparable with those of the author in the studies described under Fig. 3, i.e., clean glass surfaces and fairly non-photogenic nitrogen; addition of inert nitrogen here produces only a small increase in initial glow intensity, and the duration of the after-glow is somewhat prolonged rather than shortened, both of which might easily escape detection by ordinary visual methods.

#### *Summary.*

It is shown (i) that the introduction of a photogen *after* nitrogen has been sparked induces the after-glow in pure nitrogen, (ii) that a strong glow appears if the same gas be placed in contact with a paraffined surface, and (iii) that the amount of chemical reaction between the wax and the active nitrogen is much less in photogenic than in non-photogenic nitrogen. These observations are considered to furnish proof of the correctness of the theory that photogens are wall-poisons and convert the non-luminous heterogeneous re-association of atoms into a homogeneous reaction accompanied by emission of light. Studies are also described upon the addition of other gases to the after-glow, and the results are shown to be in accordance with the three-body collision theory of the emission of the after-glow, provided that the condition of the walls is such that they do not interfere.

The author's acknowledgments are due to Mr. W. A. Bayliss for much technical assistance in these experiments.

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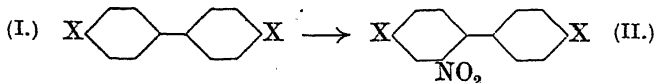
[Received, March 13th, 1930.]

CXLVII.—*Orientation Effects in the Diphenyl Series.*  
*Part VIII. The Nitration of 4:4'-Difluorodiphenyl.*

By RAYMOND JAMES WOOD LE FÈVRE and EUSTACE EBENEZER TURNER.

THE earliest papers in this series were concerned with showing that certain 4:4'-disubstituted diphenyl derivatives underwent unsymmetrical dinitration. This was notably so with the dichloro- and the dibromo-compound, each of which formed first the 2-nitro-derivative, which then gave, on further nitration, the corresponding 2:3'-dinitro-compound.\* Attention was directed to the fact that these substitutions were as nearly quantitative as possible.

At the above period, similar and comparative experiments on 4:4'-difluoro- and 4:4'-di-iodo-diphenyl had not been reported. Nevertheless it was felt that a simple application of results, obtained in other investigations of the phenomena of aromatic substitution, to the mechanism of nitration of disubstituted diphenyl derivatives consistently envisaged in this series (compare Parts I and IV) would give an accurate forecast of the facts. For instance, in a 4:4'-disubstituted diphenyl compound (I), the position in which



the first nitro-group enters is determined only by the relative powers of X and  $p\text{-X}\cdot\text{C}_6\text{H}_4$  in facilitating ortho-substitution. When X is chlorine or bromine, it happens that  $p$ -chloro- or  $p$ -bromo-phenyl easily outweighs chlorine or bromine in this respect, and the 2-nitro-derivative is therefore produced ( $I \longrightarrow II$ ). Similarly, the second entrant nitro-group is affected only by the competing ortho-facilitations of  $p\text{-X}\cdot o\text{-NO}_2\cdot\text{C}_6\text{H}_3$  and X; in the examples cited, it enters the 3'-position.

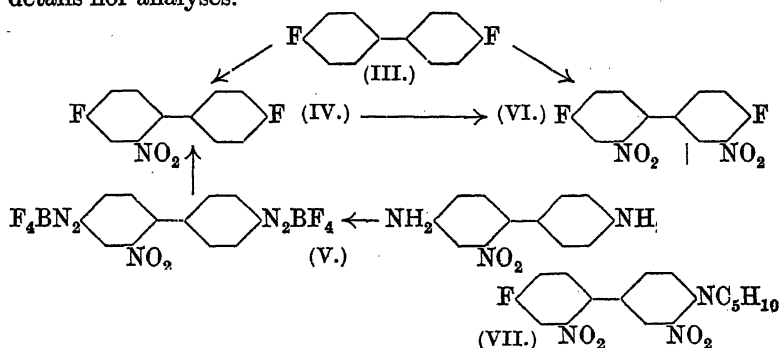
From what is known regarding the relative orienting influences of the halogens, it would be expected that 3-mononitration should become less likely as one passes down the series: 4:4'-di-iodo-, 4:4'-dibromo-, 4:4'-dichloro-, 4:4'-difluoro-diphenyl. Actually, Hodgson (J., 1926, 2384), by the dinitration of 4:4'-di-iododiphenyl, obtained only the 2:3'-dinitro-derivative, indicating that the first nitro-group enters only the 2-position. Since, therefore,

\* Borsche and Scholten (*Ber.*, 1917, 50, 609) state that the product of dinitrating 4:4'-dichlorodiphenyl is identical with the 4:4'-dichloro-2:2'-dinitrodiphenyl obtained by heating 2:5-dichloronitrobenzene with copper powder. Actually, a mixture of the two compounds concerned melts at a temperature well below the m. p. of either individual.

4 : 4'-dibromo- and -dichloro-diphenyl undergo no 3-mononitration, it seems certain that 4 : 4'-difluorodiphenyl would be nitrated quantitatively in position 2.

In the further nitration of 4 : 4'-difluoro-2-nitrodiphenyl, we should expect the second nitro-group to enter the 3'-position for three reasons: (1) By analogy with the three parallel cases in which the other halogens are present, (2) because, although it may be the weakest ortho-directing halogen, fluorine still possesses this power, and (3) because this substitution would be more open to the steric influence of the 2-nitro-group.

With these considerations before us, we had no doubt that Schiemann and Bolstad's statement (*Ber.*, 1928, **61**, 1403), that the nitration of 4 : 4'-difluorodiphenyl gives a 3-mononitro-derivative only, was inaccurate. Their evidence for this constitution was that by the action of potassium methoxide a methoxy-derivative was formed. For this, however, they give neither preparative details nor analyses.

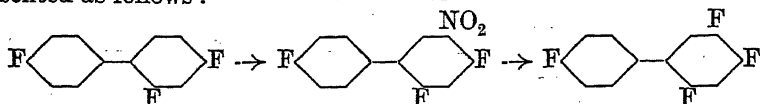


We accordingly reinvestigated this problem, with the following results: 4 : 4'-Difluorodiphenyl (III), prepared by a process analogous to but simpler than that described by Schiemann and co-workers, was shown not to react with boiling piperidine. It gave a mononitro-derivative melting at 94—95°, as described by the previous investigators. This substance did not react with boiling piperidine, and was identical with 4 : 4'-difluoro-2-nitrodiphenyl (IV) obtained by thermal decomposition of the *bisdiazonium borofluoride* (V) obtained from 2-nitrobenzidine. The mononitro-compound was therefore the 2-nitro-derivative. This conclusion was confirmed by the production, on further nitration of the mononitro-compound, of a substance (also produced by dinitration of 4 : 4'-difluorodiphenyl) which rapidly reacted with piperidine, even in the cold, to give a fluorodinitropiperidinodiphenyl. The dinitro-compound must therefore be 4 : 4'-difluoro-2 : 3'-dinitrodiphenyl (VI),

and that no appreciable quantity of any isomeride accompanies it is shown by the fact that the crude nitration product melts only  $1^{\circ}$  lower than the pure compound.

As the scheme on p. 1159 indicates, the nitration of 4 : 4'-difluoro-diphenyl follows a course exactly similar to that of the analogous chloro- and bromo-compounds.

Schiemann and Bolstad (*loc. cit.*) converted their supposed 4 : 4'-difluoro-3-nitrodiphenyl into the corresponding amino-compound and thence into a trifluorodiphenyl by the diazoborofluoride method. These two compounds must be respectively 4 : 4'-difluoro-2-amino- and 2 : 4 : 4'-trifluoro-diphenyl. Schiemann and Roselius (*Ber.*, 1929, 62, 1805) nitrated the trifluoro-compound, reduced the product, and again replaced the amino-group by fluorine. Their evidence for the constitution of the trifluoronitrodiphenyl consisted in showing that the derived tetrafluorodiphenyl was oxidised to *p*-fluorobenzoic acid, and they accordingly regarded it as 3 : 4 : 5 : 4'-tetrafluorodiphenyl. Accepting the evidence of oxidation, it seems probable that the reactions in question are more correctly represented as follows :



but further investigation appears desirable.

#### EXPERIMENTAL.

**4 : 4'-Difluorodiphenyl.**—The method described by Balz and Schiemann (*Ber.*, 1927, 60, 1186) for the replacement of amino-groups by fluorine atoms considerably simplifies this process. We have found that the difficultly accessible hydroborofluoric acid may be replaced by the readily obtainable sodium borofluoride. The following method gave excellent results : A solution of benzidine (46 g.) in concentrated hydrochloric acid (150 c.c.) and water (150 c.c.) was bisdiazotised, a solution of 35 g. of sodium nitrite in 60 c.c. of water being used and 200 g. of ice added during the process. The solution was filtered and added to a filtered solution of 85 g. of sodium borofluoride in 150 c.c. of water. On stirring, the bisdiazonium borofluoride separated in cream-coloured needles ; a further quantity was obtained on addition of more sodium borofluoride. The precipitate was collected, dried at  $100^{\circ}$ , and decomposed by being heated in an open flask, fitted with an air-condenser, the temperature being slowly raised to  $150^{\circ}$ . Steam distillation of the product gave 21 g. of pure difluorodiphenyl. After being crystallised from alcohol, it had m. p.  $92-93^{\circ}$ .



*Mononitration of 4:4'-Difluorodiphenyl.*—A solution of 5 g. of difluorodiphenyl in 10 c.c. of warm glacial acetic acid was cooled and treated with a mixture of 7 c.c. of nitric acid of *d* 1.4 and 2 c.c. of nitric acid of *d* 1.52. The whole was left over-night, then warmed to 60°, cooled, and glacial acetic acid added; 4.5 g. of a product, m. p. 85—95°, were obtained. After crystallisation from light petroleum-benzene, the substance had m. p. 94—95°. The 4:4'-difluoro-2-nitrodiphenyl so obtained depressed the m. p. of 4:4'-difluorodiphenyl (Found: C, 61.4; H, 2.9; N, 6.1. Calc.: C, 61.3; H, 3.0; N, 6.0%). The nitro-compound was recovered unchanged from a piperidine solution which had been boiled for several minutes.

*4:4'-Difluoro-2-nitrodiphenyl.*—2-Nitrobenzidine (11.5 g.) was warmed with 35 c.c. of concentrated hydrochloric acid until it was completely converted into the hydrochloride; 30 c.c. of water were then added. The suspension was bisdiazotised (7 g. of sodium nitrite in 12 c.c. of water) and the solution was filtered and added to a filtered solution of 30 g. of sodium borofluoride in 50 c.c. of water. After a few minutes, 2-nitro-4:4'-diphenylbisdiazonium borofluoride separated as matted needles which, after being dried at 100°, became a yellow sandy powder; this turned brown at about 125° and decomposed with effervescence at 129° (Found: N, 16.5.  $C_{12}H_7O_2N_5F_3B_2$  requires N, 16.4%).

Conversion of the diazonium borofluoride into the difluoronitrodiphenyl was effected by mixing it with fine purified sand, or with barium sulphate, and heating gradually in a bath to 190°, the whole operation occupying  $\frac{1}{2}$  hour. The mixture obtained was distilled in steam, and the cooled distillate filtered. The 4:4'-difluoro-2-nitrodiphenyl so isolated melted at 94—95°, either alone or when mixed with the substance obtained by the nitration of difluorodiphenyl (Found: N, 6.4, 6.3. Calc.: N, 6.0%).

*Dinitration of 4:4'-Difluorodiphenyl.*—The difluorodiphenyl (2 g.) was gradually added to 15 c.c. of nitric acid (*d* 1.5), kept cool in tap water. The solution was warmed to 100° during 5 minutes, cooled slightly, and treated with 2 vols. of glacial acetic acid and a little water. On being kept, it deposited crystals, which, after being crystallised from diluted acetic acid, formed cream-coloured leaflets, m. p. 109—110° (Found: C, 51.4; H, 2.1; N, 9.7.  $C_{12}H_6O_4N_2F_2$  requires C, 51.4; H, 2.1; N, 10.0%).

*Mononitration of 4:4'-Difluoro-2-nitrodiphenyl.*—(a) The nitro-compound obtained from 2-nitrobenzidine was added to 20 parts of nitric acid (*d* 1.5), the solution obtained being heated to 100° during 5 minutes. On cooling, crystallisation set in. Glacial acetic acid was added, the whole warmed, and then allowed to cool slowly. The dinitro-compound so obtained was crystallised from diluted

acetic acid, and then melted at 109—110°, either alone or when mixed with the product of the same m. p. described above.

(b) The mononitration product of difluorodiphenyl was gradually added to 20 parts of nitric acid (*d* 1.5), and the solution was slowly heated to 100° during 5 minutes. An equal volume of glacial acetic acid was now added, and then water, until no further precipitation occurred. The crude filtered and washed product melted at 108—109°. Crystallisation from diluted acetic acid raised the m. p. to 109—110°. A mixture of this substance with the dinitration product of difluorodiphenyl also melted at 109—110°.

*Action of Piperidine on 4:4'-Difluoro-2:3'-dinitrodiphenyl.*—A solution of the dinitro-compound (2 g.) in 5 c.c. of piperidine was boiled for 2 minutes to complete the reaction which began in the cold. Water was added and the solid precipitated was crystallised from alcohol, 4-fluoro-2:3'-dinitro-4'-piperidinodiphenyl being obtained as orange rhombohedra, m. p. 126.5—127.5° (Found: C, 59.0; H, 4.6; N, 12.2.  $C_{17}H_{16}O_4N_3F$  requires C, 59.1; H, 4.6; N, 12.2%).

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## CXLVIII.—*Studies in "Strainless" Rings. Part II.* *The Effect of the trans-Decalin Nucleus on the Carbon Tetrahedral Angle.*

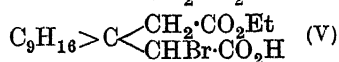
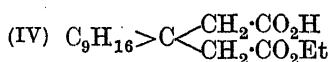
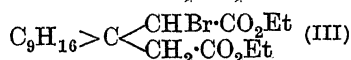
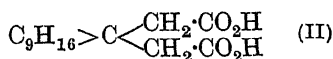
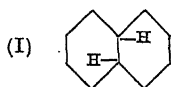
By KESHAVIAH ASWATH NARAIN RAO.

PERHAPS the most successful attempt that has been made to explain the numerous discrepancies in the relative ease of formation and the stability of different types of ring, for which Baeyer's simple conception of strain failed to account satisfactorily, is that of Thorpe and Ingold, on the basis of their "valency-deflexion" hypothesis, which rests on the fundamental assumption that, when the normal angle between two of the valencies of a carbon atom is changed through any cause, *e.g.*, their inclusion in a ring, the other two valencies apparently take up an altered relative position; more definitely, the hypothesis suggested that when the angle between two of the valencies is greater than the normal angle, the angle between the other two valencies will be less than this amount, and *vice versa* (J., 1915, 107, 1080; 1922, 121, 650, etc.). Experimental investigation has in general given very good support to the hypothesis.

It seemed desirable, therefore, to examine the rings of dicyclic

compounds on the basis of this hypothesis with the view of gaining an insight into the condition of strain in such rings.

The discovery that five- and six-membered rings can unite together by their *cis*- as well as by their *trans*-valencies satisfied the requirements of Mohr's hypothesis with regard to isomerism. But it is unsound to conclude from the fact of the existence of these isomerides that they are necessarily strainless. As Haworth (*Ann. Reports*, 1927, 24, 98) has pointed out, the existence of this type of isomerism is in no way inconsistent with the supposition that the isomerides are in a state of strain. *trans*-Decalin [decahydronaphthalene] (I), being the most interesting substance from this point of view, has been chosen in the first instance for examination. If it consists of two uniplanar and strained *cyclohexane* rings interlocked in the ortho-position, and is in consequence itself highly strained, there should be no difference between the effects of *trans*-decalin and *cyclohexane* on the carbon tetrahedral angle; if, on the contrary, it relieves its strain by causing the component *cyclohexane* rings to assume multiplanar and strainless forms, its effect

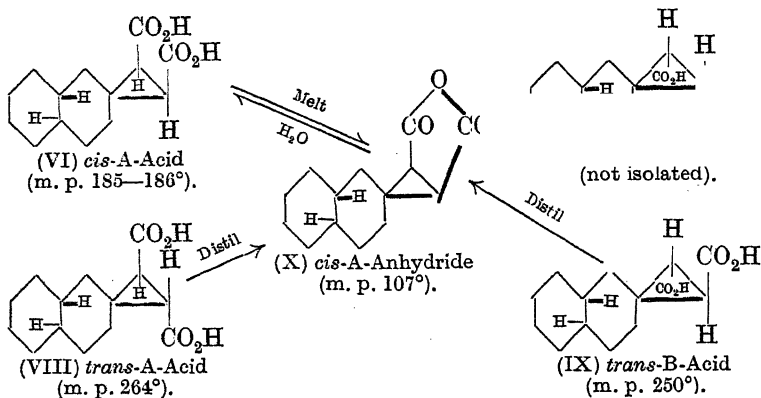


should be similar to that of *cyclopentane* on this angle. The experiments which have been carried out on derivatives of *trans*-decalin-2:2-diacetic acid (II) prove conclusively that *trans*-decalin relieves its strain almost completely, diminishing in consequence the convergence of the two acetic acid residues towards each other.

As in the *cyclohexane* and *cycloheptane* series, it has not been possible to prepare the *monobromo-ester* (III) by bromination of *trans*-decalin-2:2-diacetic acid. The ester is, however, readily prepared by bromination of *ethyl hydrogen trans-decalin-2:2-diacetate* (IV); but it cannot be purified, since it undergoes partial conversion into the lactonic ester on distillation. Some *monobromo-acid ester* (V) is always formed during the bromination. On hydrolysis with concentrated aqueous potassium hydroxide, the neutral and the acid products of bromination lose hydrogen bromide and form the stereoisomeric *spiro-cyclopropane acids*, the yield, about 38% of the theoretical, being the same as in the *cyclohexane* and *cycloheptane* series. The remainder of the material is converted into a mixture of lactonic acids.

*trans*-Decalin- $\beta$ -*spiro-cyclopropane*-1:2-dicarboxylic acid can

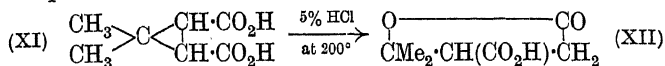
exist in four stereoisomeric forms, two *cis*- (VI and VII) and two *trans*- (VIII and IX). Three of these (the *trans*-A- and -B-acids and the *cis*-A-acid) have been isolated from the products of hydrolysis



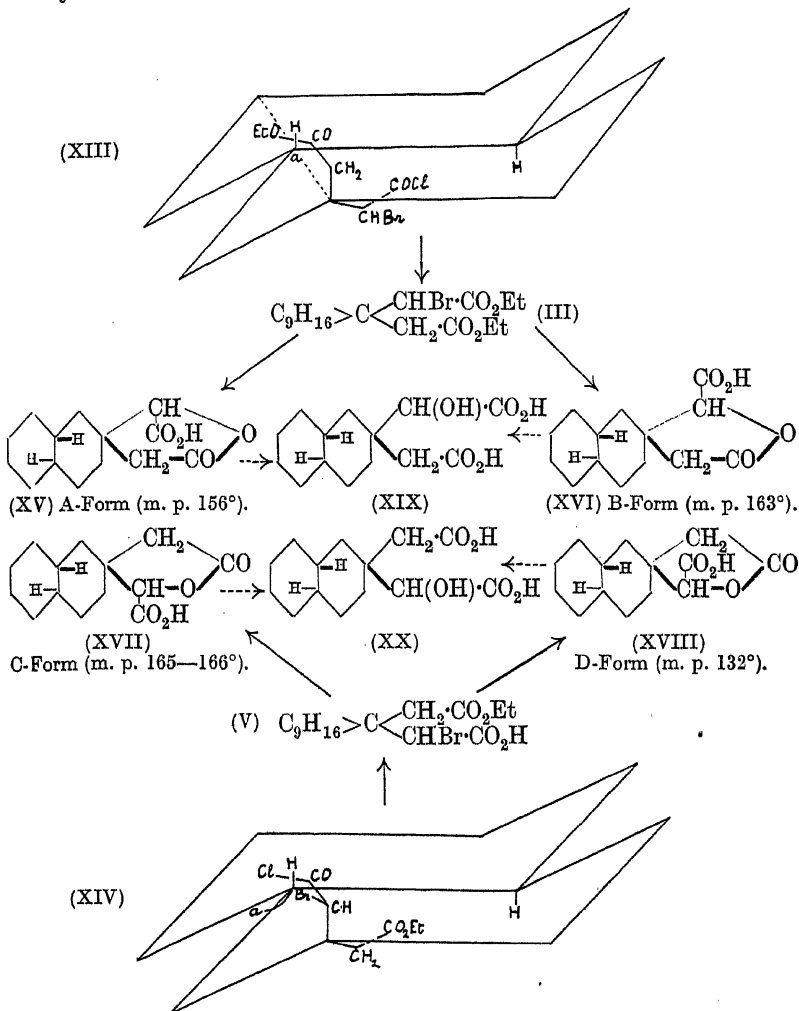
of the neutral and the acid monobromo-esters. The mixture of *trans*-spiro-acids has been separated by repeated fractional crystallisation from aqueous acetone into two acids: (1) the less soluble *A*-acid (VIII), which, as thus obtained, is amorphous, and (2) the more soluble *B*-acid (IX), which is highly crystalline. The two *trans*-spiro-acids should give rise to a mixture of the *cis*-acids (A) and (B) by the directional change of either of the carboxyl groups. Although evidence of the formation of a mixture of *cis*-anhydrides by the distillation of these acids—the *trans*-acids are unchanged on melting—has been obtained, only the *cis*-A-anhydride (X) can be obtained pure from the mixture. The *cis*-A-acid (VI) is formed by hydration of the *cis*-anhydride.

It is in the stability of these *trans*-spiro-acids that the remarkable difference between *trans*-decalin and *cyclohexane* in their effects on the carbon tetrahedral angle is revealed. Both the *trans*-spiro-acids from *trans*-decalin are equally stable (or unstable) towards hydrochloric acid, thus demonstrating that the stability of the spiran-structure depends almost entirely on the ring with which it is associated and very little on other factors. They are unattacked by 5% hydrochloric acid at 240° and by 10% acid at 200°, but are completely decomposed by the latter at 240°; 20% acid decomposes them at a much lower temperature, *viz.*, 200°, within two hours: the *cyclohexane* analogue is unaffected by concentrated hydrochloric acid at 240° during several hours. No definite substance can, however, be isolated, carbon being the chief product of such a decomposition. It is remarkable that of all the analogous compounds, caronic acid (XI) should be the only one to give a definite

product of decomposition, *viz.*, terebic acid (XII). That the observed decomposition of the *trans*-*spiro*-acids is due to the instability of



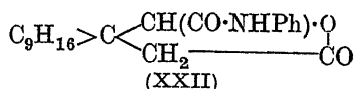
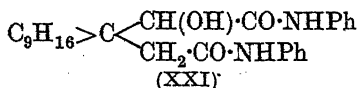
the *spiro*-cyclopropane ring and not of *trans*-decalin *per se* is proved by the fact that *trans*-decalin-2 : 2-diacetic acid, after being subjected



to similar treatment, is recovered unchanged. The *spiro*-acids are stable to cold acid or alkaline permanganate and are decomposed only after prolonged boiling.

It has already been shown (Rao, J., 1929, 1954) that in *cis*- and *trans*-decalins of the type  $C_9H_{16} > C \begin{smallmatrix} X \\ < \\ Y \end{smallmatrix}$  only one isomeride corresponding to each decalin is formed when X and Y are identical or are replaced by a symmetrical ring. Further, when X and Y are different, two isomerides (A and B) corresponding to each decalin are obtained, the replacement of X and Y by an unsymmetrical ring not causing any reduction in the number of isomerides. It is therefore to be expected that, when a monosubstituted unsymmetrical ring takes the place of X and Y, four isomerides from each decalin will be produced. This expectation has been realised in the case of *trans*-decalin, for, when the neutral and the acid monobromo-ester (III and V respectively) are hydrolysed with aqueous sodium carbonate, the four stereoisomeric lactones of  $\alpha$ -hydroxy-*trans*-decalin-2 : 2-diacetic acids are formed.

The neutral monobromo-ester (III) is converted into the two lactones (A) and (B), the acid monobromo-ester (V) into two other stereoisomerides (C) and (D). The formation of two different pairs of lactones from the two bromo-esters is probably due to the different configurations of the latter. On examining the model of *trans*-decalin-2 : 2-diacetic acid, it is found that the two carboxyl groups are not equidistant from the tertiary carbon atom ( $\alpha$ ), which is in the  $\beta$ -position to the carbon attached to the acetic acid residues. Two bromo-acid chlorides (XIII and XIV) are formed from the stereoisomeric acid esters (IV). In one of these (XIV), the hydrogen attached to the tertiary carbon atom  $\alpha$ , the bromine, and the acid chloride group are all crowded into a small volume, resulting probably in the development of some sort of steric hindrance. This would resist any further crowding such as would be caused by the introduction of an ethyl group in place of the chlorine. The latter would therefore undergo preferential replacement by hydroxyl, the bromo-acid ester being formed. This would give rise to the two lactones (XVII and XVIII). On the other hand, there is no such abnormal condition in the stereoisomeric bromo-acid chloride (XIII), which would therefore form the neutral ester easily; this neutral bromo-ester forms the two other lactones (XV and XVI).



It was intended to confirm the correctness of this interpretation by the formation of the dianilides (XXI) of the parent hydroxy-acids (XIX and XX) by the interaction of the lactones with aniline.

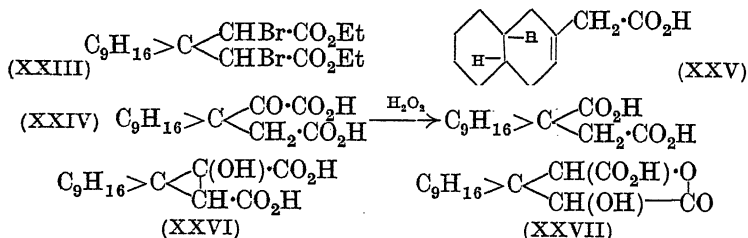
Lactones (A) and (B), which are descended from the hydroxy-acid (XIX), would give one dianilide, different from that produced from the acid (XX) formed from the lactones (C) and (D). But unfortunately all the lactones are converted into their *monoanilides* (XXII) on being heated with *excess* of aniline at 200—220°. The uniform stability of the *spiro-cyclopentane* (heterocyclic) ring in all the isomerides is but another illustration of the stability of the *spiro-cycloid* being dependent only on the ring with which it is associated.

The formation of the *monoanilides* illustrates an interesting difference between *trans*-decalin and *cyclohexane*, where the dianilide is easily formed by the action of aniline on the lactones at 200°. Since the internal angle of *trans*-decalin (which is a strainless ring) is very nearly the same as the normal angle, the angle between the extracyclic valencies would be of nearly the same value. While this angle (*ca.* 109·5°) makes the associated *cyclopropane* ring (which requires an angle of 60° for stability) unstable (as illustrated by the instability of the *spiro-cyclopropane* acids), it is of the optimum value for the formation of a stable *cyclopentane* ring (stability of the lactones). In *cyclohexane*, on the contrary, the angle between the extracyclic valencies is 107·2°, which is less than the normal angle. This angle increases the stability of *spiro-cyclopropane*, but has a reverse effect on the stability of the associated *cyclopentane*, since it causes the distance between the terminal carbon atoms to increase through overlapping. The work of Dickens, Kon, and Thorpe (J., 1922, **121**, 1499) on *cyclopentanediones* and of Sircar (J., 1927, 1253) on the stability of heterocyclic compounds also illustrates this progressive decrease in stability due to the increased distance between the terminal carbon atoms through overlapping.

So far as the author is aware, this is the first instance in this type of dicyclic ring of the preparation of four stereoisomerides from one parent. Their existence is in complete harmony with Mohr's hypothesis. Orientation of these isomerides is not possible, as there is no known method by which this can be accomplished.

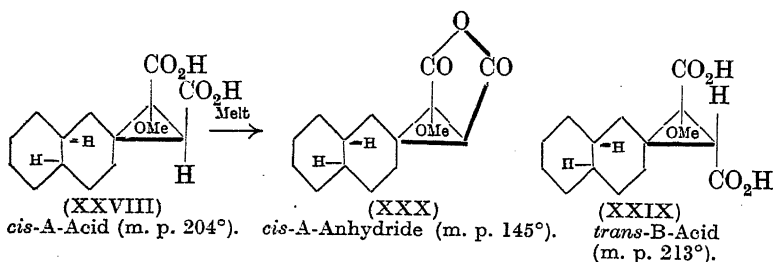
The *dibromo-ester* (XXIII) is readily prepared by the dibromination of *trans*-decalin-2 : 2-diacetic acid, very little acid product being formed when the bromination is carried out under strictly defined conditions. The remarkable difference between *cyclohexane* and *trans*-decalin is again clearly demonstrated by a study of the hydrolysis of the *dibromo-ester* with potassium hydroxide. When ethyl *trans*-decalin-2 : 2-dibromoacetate is hydrolysed with 64% aqueous potassium hydroxide, there is formed mainly (49%)  $\alpha$ -*keto-trans*-decalin-2 : 2-diacetic acid (XXIV), together with a

small quantity (under 4%) of the unsaturated acid (XXV). No trace of the hydroxy-*spiro*-acid (XXVI) could be detected. The



rest of the material is converted into a mixture of the stereoisomeric hydroxy-lactonic acids (XXVII), which cannot be induced to solidify even after 12—18 months. Hydrolysis of the dibromo-ester with 15% sodium hydroxide does not yield any unsaturated acid.

When methyl-alcoholic potash is used for the hydrolysis, the dibromo-ester is converted into a mixture of *cis*- and *trans*-methoxy-*spiro*-acids (XXVIII and XXIX respectively).



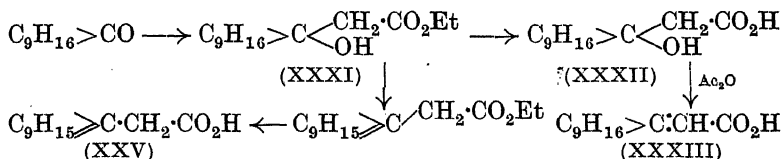
The two acids probably do not belong to the same series, because their melting points lie very close to each other and, moreover, it has not been possible to convert the *trans*-acid into the *cis*-isomeric, which readily gives an *anhydride* (XXX) on melting. The *trans*-methoxy-*spiro*-acid (XXIX) is converted into the keto-acid (XXIV) on boiling with hydrobromic acid. The hydroxy-*spiro*-acid (XXVI) is undoubtedly first formed by the hydrolysis of the methoxy-group, but as soon as the necessary mobile hydrogen atom is introduced into the system the ring acid is converted into the stable open-chain isomeric. The stability of the latter is further demonstrated by the fact that after boiling for 4 hours in 64% potassium hydroxide solution, it is recovered entirely unchanged.

It may be recalled that, in the *cyclohexane* series, considerable quantities of hydroxy-*spiro*-acid (type XXVI), unsaturated acid (type XXV), and hydroxy-lactonic acid (type XXVII) were formed by the hydrolysis of the dibromo-ester (or its bromo-lactones);



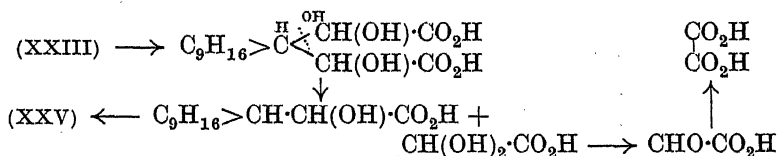
no keto-acid (type XXIV) was formed during the change. In the *cyclopentane* series, on the other hand, the main product of the hydrolysis was the keto-acid (type XXIV), small quantities of *cyclopentylideneacetic acid* (type XXXIII) and the hydroxy-lactonic acid also being formed; no hydroxy-*spiro*-acid was encountered. When methyl-alcoholic potash was used for the hydrolysis, however, a mixture of the hydroxy-*spiro*-acid and its methoxy-derivative was produced, both of which were completely converted into the keto-acid on hydrolysis with hydrobromic acid; moreover, the hydroxy-*spiro*-acid was found to be a *cis*-acid, unlike analogous compounds in the other series. Finally, in the *cycloheptane* series, the product of hydrolysis of the dibromo-ester with aqueous potash consisted of about 90% of the hydroxy-lactonic acid, 3% of the hydroxy-*spiro*-acid, and 7% of the *cycloheptylideneacetic acid* (type XXXIII); the hydroxy-*spiro*-acid or its methoxy-derivatives pass into the keto-acid (99%) on hydrolysis with hydrobromic acid.

*trans*- $\beta$ -Decalone condenses with ethyl bromoacetate in presence



of zinc to form the *hydroxy*-ester (XXXI), which on dehydration and subsequent hydrolysis is converted into  $\Delta^{2(\text{or } 1)}$ -*trans-octa-hydronaphthalene-2-acetic acid* (XXV), identical with the unsaturated acid obtained by the hydrolysis of the dibromo-ester. *trans-Decahydronaphthylidene-2-acetic acid* (XXXIII) is prepared by dehydration of the *hydroxy*-acid (XXXII). That the  $\alpha\beta$ -acid is first formed during the hydrolysis of the dibromo-ester and is subsequently converted into the  $\beta\gamma$ -isomeride by the strong alkali has been proved by boiling a solution of the former in 64% potash, whereby it is completely converted into the  $\beta\gamma$ -acid.

The formation of the unsaturated acid from the dibromo-ester probably involves the elimination of one of the (hydroxy)acetic

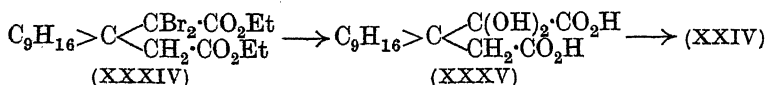


acid residues as glyoxylic acid, which is then oxidised to oxalic acid (see J., 1915, 107, 1080). The last-named substance arising from

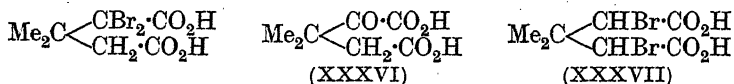
this oxidative fission has actually been isolated from the products of hydrolysis.

Hydrolysis of the dibromo-ester (XXIII) with aqueous sodium carbonate produced a mixture of acids from which a crystalline substance, m. p. 182—183°, having properties usually associated with hydroxy-lactonic acids, was isolated, but the quantity obtained was too small for investigation. From the rest of the material, which showed no tendency to crystallise during several months, small quantities of the keto-acid were isolated by various methods; no other solid product was obtained.

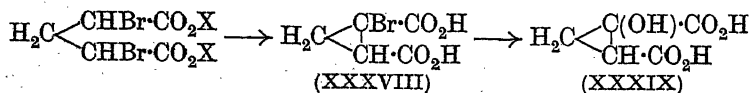
The explanation of this unexpected formation of the keto-acid by the sodium carbonate hydrolysis of the dibromo-ester is not immediately obvious. One simple way is to assume that the product of dibromination is really an unsymmetrical dibromo-ester (XXXIV). This, on replacement of the bromine atoms by hydroxyl, would give the dihydroxy-compound (XXXV), which is the hydrated



form of the keto-acid. But, although numerous substituted glutaric acids have been brominated, in no case has the formation of an unsymmetrical dibromo-derivative been observed. The one substance, *viz.*, ethyl hydrogen dibromo- $\beta\beta$ -dimethylglutarate (Perkin and Thorpe, J., 1901, 79, 729), which was assumed to be of such a type because it gave the keto-acid (XXXVI) on hydrolysis with alkali, was later considered by Kon, Stevenson, and Thorpe (J., 1922, 121, 657) to be the  $\alpha\alpha'$ -dibromo-derivative (XXXVII).



The explanation must therefore be sought in another direction. Ingold (J., 1921, 119, 314) has shown that the sequence of changes, dibromo-ester  $\longrightarrow$  bromo-ring acid  $\longrightarrow$  keto-acid, takes place in presence not only of alkali hydroxide but also of sodium carbonate. It was found that when methyl, ethyl, or *isopropyl* dibromoglutarate was hydrolysed by 2*N*-sodium carbonate a small quantity of the bromocyclopropanedicarboxylic acid (XXXVIII) was produced. On prolonged boiling, however, replacement of the bromine



atom by hydroxyl occurred, with the formation of cyclopropanoldicarboxylic acid (XXXIX).

Such a change is what in all probability occurs in the present instance. It was found necessary to boil the dibromo-ester with a solution of sodium carbonate (saturated at 105°) during 60 hours, before there was appreciable hydrolysis. Under these conditions, the hydroxy-ring acid (XXVI) would be first produced, and, being unstable, be immediately converted into the keto-acid (XXIV).

The hypothetical existence of the two multiplanar forms of cyclohexane, (a) the "boat" (XL) and (b) the "arm-chair" (XLI), may be assumed to explain the formation of decalin. The "boat"



is a loose shape which cannot pass into the other form without strain, but is itself capable of passing through a series of vibrating phases by strain-free relative rotations. The number of decalins that can exist by a combination of these forms through their *cis*- as well as their *trans*-valencies is large. But Mohr's postulate is probably applicable, and then all the *cis*-forms can be reduced to one configuration, and the *trans*- to another (Wightman, J., 1925, 127, 1421; Hückel, "Fortschritte der Chemie, Physik und Physikalischen Chemie," Bd. 19, Heft 4, 1927, 27—30). All these forms are probably different phases (the decalin made of two uniplanar cyclohexanes is probably one of these, though of much shorter duration) of the vibrating molecule, no phase having more than a transitory existence. The substance behaves stereochemically as if its configuration were the average condition of the limiting states. Moreover, the further the uniplanar form departs from the strainless phase, the more will the molecule behave as a strainless ring.

On examining a model of *trans*-decalin, it is readily seen that it would be very greatly strained if the component cyclohexanes were uniplanar; on the other hand, almost complete relief of this strain takes place if the two rings are multiplanar. *trans*-Decalin should therefore be expected to behave like a strainless ring, and this is exactly what has been demonstrated by the present investigation. The instability of the *spiro*-cyclopropane acids, the non-existence of the hydroxy-ring acid, and the stability of the keto-acid all show that *trans*-decalin occupies a place in the table midway between cyclopentane and cycloheptane, rather than near cyclohexane. This evidence is in perfect agreement with that from other sources, including the measurement of the heats of combustion (Roth and Lassé, *Annalen*, 1925, 441, 48).

Brief reference may be made to the strain in *cyclohexane* which has been the subject of controversy in recent years (Hückel, *op. cit.*). The non-existence of two stable strainless forms (Wightman, J., 1926, 2541; Werner and Conrad, *Ber.*, 1899, **32**, 3046) which would be expected on the basis of Sachse's hypothesis (*Ber.*, 1890, **23**, 1363) was explained by Mohr (*J. pr. Chem.*, 1918, **98**, 315; 1922, **103**, 316) by assuming that the temporary strain involved in the interconversion of Sachse's strain-free structures is sufficiently slight to be overcome by forces due to molecular cohesion; yet the fact remains that there is no experimental proof whatever of the existence of strainless *cyclohexane*. Moreover, the data obtained from X-ray examination (Hendricks and Bilicke, *J. Amer. Chem. Soc.*, 1926, **48**, 3007) of benzene hexahalides do not indicate the existence of a multipplanar *cyclohexane*. It has been argued that because decalin exists in *cis*- and *trans*-forms and may therefore be considered fairly free from strain, *cyclohexane* itself should lie in more than one plane. There is no justification for this view, because the condition which exists in dicyclic compounds, *e.g.*, *trans*-decalin, where the strain would be very great if the component *cyclohexanes* were uniplanar, is quite different from that in *cyclohexane*, where the strain would not be excessive.

Hückel (*op. cit.*, p. 90) contends that the "valency-deflexion" hypothesis "steht und fällt mit der willkürlicher Annahme eines ebenen gespannten Sechsrings" and suggests, "eine weitere Ausdehnung des Vergleichs auf substituierte Cyclohexanringe und auf Derivate des *trans*-Dekalins, in denen der Sechsring sicher nicht eben sein kann, wäre von Bedeutung." The marked contrast in the effects of *cyclohexane* and *trans*-decalin on the carbon tetrahedral angle demonstrated by this investigation, which was begun long before Hückel's publication appeared, can only be due to a large difference in strain in the two rings; it should be noted that the polar influences, whatever their nature, would be expected to be similar in the two rings. *trans*-Decalin is obviously strainless, on the evidence from all sources; it seems probable, therefore, that the average condition of the vibrational limits of *cyclohexane* possesses appreciable strain.

One of the characteristics of the analogous derivatives of *cyclopentane* (Becker and Thorpe, J., 1920, **117**, 1584) and *cycloheptane* (Baker and Ingold, J., 1923, **123**, 127) is their remarkable lack of tendency to crystallise. The derivatives of *trans*-decalin display this characteristic even more prominently. This, and the formation of a number of stereoisomerides in all the reactions, has made the experimental investigation extremely difficult. None of the substances described in this paper can be accumulated in any con-

siderable quantity, and even their isolation is possible only when the directions given in the experimental part are closely followed.

# EXPERIMENTAL.

*Ethyl Hydrogen trans-Decalin-2:2-diacetate* (IV).—A solution of sodium (35 g.) in absolute ethyl alcohol (500 c.c.) was added slowly with stirring to a solution of the anhydride of *trans*-decalin-2:2-diacetic acid (356 g.), also dissolved in absolute ethyl alcohol (175 c.c.). After the reaction became slow, the alcohol was removed in a vacuum, and the aqueous solution of the sodium salt acidified with dilute hydrochloric acid. The heavy oil which was precipitated was extracted with pure ether, dried thoroughly, recovered, and kept at 100° under vacuum for 1 hour (420 g.). The *acid ester* [Found: equiv., 280.  $C_{10}H_{16}(CH_2 \cdot CO_2Et) \cdot CH_2 \cdot CO_2H$  requires equiv., 282] is a thick, almost colourless syrup; on distillation under reduced pressure, it is reconverted into the anhydride.

Methyl hydrogen *trans*-decalin-2:2-diacetate was prepared in a similar way (Found: Ag in the *silver* salt, 27.0.  $C_{15}H_{23}O_4Ag$  requires Ag, 28.8%).

*Monobromination.* When the ethyl acid ester (420 g.) was cautiously mixed with phosphorus pentachloride (330 g.), a vigorous reaction occurred and hydrogen chloride was evolved: the conversion into the acid chloride was completed by heating on the steam-bath for 1 hour. Dry bromine (82 c.c.; 1.1 mols.) was then added portionwise during 6 hours, the mixture being kept at 50—60°. When the evolution of hydrogen bromide had ceased, the whole was poured into absolute ethyl alcohol (2 l.), kept at 25°. After the vigorous reaction had subsided, the solution was boiled for  $\frac{1}{2}$  hour and then mixed with excess of water. The precipitated bromo-ester was extracted with ether, the acid product removed with a 5% solution of sodium carbonate, and the extract then dried over calcium chloride and evaporated. The residual neutral *monobromo-ester* (III) was kept over concentrated sulphuric acid in a vacuum during several days (yield, 80—83%) (Found: Br, 19.1.  $C_{18}H_{29}O_4Br$  requires Br, 20.5%). On distillation even under 2 mm., it (b. p. 180—200°/2 mm.) was partly converted into the lactonic ester, the distillate being a thick viscid syrup (Found: C, 61.9; H, 8.2. The lactonic ester,  $C_{16}H_{24}O_4$ , requires C, 68.6; H, 8.6%. The monobromo-ester,  $C_{18}H_{29}O_4Br$ , requires C, 53.7; H, 7.2%).

The acid product of the monobromination extracted by aqueous sodium carbonate (above) was obtained as a heavy oil on acidification (yield, 17—20%); it could not be purified by distillation (Found: Br, 21.6.  $C_{16}H_{25}O_4Br$  requires Br, 22.1%). This acid

monobromo-ester is formed even under conditions most conducive to the complete esterification of the bromo-acid chloride.

*Stereoisomeric Lactones of  $\alpha$ -Hydroxy-trans-decalin-  
2 : 2-diacetic Acids.*

*Lactones (A) (XV) and (B) (XVI).*—These lactones are the only products of the action of boiling sodium carbonate solution on the neutral monobromo-ester (III). A suspension of the mixture of the monobromo-ester and lactonic ester (30 g.), obtained by the distillation of the monobromo-ester, in a solution (saturated at 105°) of sodium carbonate (60 g.) was boiled for 72 hours. The solution was diluted and extracted with ether to remove any unchanged ester. The oil precipitated on acidification was thrice extracted with pure ether, dried, recovered, and kept at 90° for 2 hours. After remaining for 2 weeks in a vacuum over sulphuric acid, it was dissolved in benzene, to which was then added as much light petroleum (b. p. 60—80°) as possible without producing a turbidity. The solid which had separated during 1 week was collected (A). On further addition of light petroleum to the filtrate, an oil (B) was precipitated, from which the supernatant liquid was poured off.

After several months, the mother-liquor deposited colourless nodules. These separated from benzene-light petroleum (b. p. 60—80°) in crystalline lumps, m. p. 137—140°. Titration with *N*/20-barium hydroxide showed that this substance was a mixture of lactone and the hydroxy-acid; the latter, however, could not be obtained sufficiently pure for analysis.

*Lactone (A)* crystallised from benzene in colourless silky needles, m. p. 156° (Found: C, 66.7; H, 7.9; equiv., by titration with *N*/20-barium hydroxide, 256.  $C_{14}H_{20}O_4$  requires C, 66.7; H, 7.9%; equiv., for monobasic acid, 252).

When concentrated aqueous solutions of the lactone and aniline were mixed, the *aniline* salt separated in long silky needles, m. p. 126° (Found: C, 69.1; H, 7.9.  $C_{14}H_{20}O_4 \cdot C_6H_5 \cdot NH_2$  requires C, 69.6; H, 7.8%).

The lactone and excess of aniline were heated together at 200—210° for 1.5 hours. The gum obtained on cooling was triturated with dilute hydrochloric acid; it then solidified. Crystallised from dilute ethyl alcohol, the *monoanilide* separated in long, colourless, feathered needles, m. p. 154° (Found: C, 73.4; H, 7.8; N, 4.5.  $C_{20}H_{25}O_3N$  requires C, 73.4; H, 7.6; N, 4.3%).

*Lactone (B) (XVI).* The oil (B, above) solidified after some weeks and then separated from benzene in stellate clusters of soft needles, m. p. 163° (Found: C, 66.6; H, 8.1%; equiv., 252). It is sparingly

soluble in cold benzene. A mixture of lactones (A) and (B) melts at 123—125°.

The *aniline* salt of lactone (B) crystallised from benzene in long silky needles, m. p. 147° (Found : C, 69.6; H, 7.5%). The *monoanilide* separated from dilute methyl alcohol in dirty white, spherical nodules, m. p. 172° (Found : C, 73.2; H, 7.9; N, 4.5%).

*Lactones (C) (XVII) and (D) (XVIII).*—A sodium carbonate solution (25 g. in 225 c.c. of water) of the acid bromo-ester (V) (40 g.) was boiled for 8 hours, diluted and acidified, and the precipitated oil collected in ether. The ethereal solution having been partly dried over calcium chloride, the substance (29 g.) was recovered : it showed no signs of crystallising and therefore was esterified with ethyl alcohol (120 c.c.) and concentrated sulphuric acid (12 c.c.). The product was isolated in the usual way and after two fractional distillations in a vacuum was separated into two fractions : (1) 210—211°/6 mm., (2) 215°/6 mm.

*Lactone (C).* The ethyl ester, b. p. 210—211°/6 mm., was boiled with concentrated hydrochloric acid for 10 hours. (The hydrolysis of the esters of these acids with hydrochloric acid is extremely slow, chiefly owing to their insolubility in the acid.) The residue obtained on removal of the acid was dried at 90° for 2 hours and dissolved in benzene-light petroleum (b. p. 60—80°). Even after 10 weeks, only a small quantity of the crystalline lactone (m. p. 110°) had separated. On recrystallisation from benzene-light petroleum (b. p. 60—80°), the lactone (C) separated in hard granular cubic masses of thick plates, m. p. 164°. These are hydrated and the anhydrous *lactone (C)*, m. p. 165—166°, is obtained from them by heating at 100° (Found : C, 66.4; H, 8.0%; equiv., 255). This lactone is sparingly soluble in both hot and cold benzene. In admixture with lactone (A) or (B), its m. p. is depressed by 20—30°.

The *monoanilide* crystallised from dilute ethyl alcohol in shimmering leaflets, m. p. 166° (Found : N, 4.4%).

*Lactone (D).* The ethyl ester, b. p. 215°/6 mm., was boiled with concentrated hydrochloric acid for 8 hours and the lactonic acid produced was isolated in the usual way, dried, and dissolved in benzene-light petroleum (b. p. 60—80°). After 8 weeks, during which time a small quantity of light petroleum was added daily to prevent turbidity in the solution, the *lactone (D)* which had been deposited was collected and recrystallised from benzene; it then separated in short colourless needles, m. p. 132° (Found : C, 66.5; H, 8.0; equiv., 249).

The *aniline* salt crystallised from benzene in silky needles, m. p. 122°.

*Hydrolysis of the Neutral Monobromo-ester with Concentrated Potassium Hydroxide Solution at 150°.*—A solution of potassium hydroxide (450 g.) in water (250 c.c.) was evaporated until the boiling point reached 150°. The bromo-ester (150 g.) was then added to the boiling solution as rapidly as possible. The reaction was not vigorous, but after 15–20 minutes' boiling the ester dissolved; at the same time a potassium salt separated. The solution was then diluted freely with water and acidified while hot. The precipitated oil was extracted from the cold solution, partly dried over calcium chloride, recovered, and dried at 90° for 3 hours. The mixture of acids (80 g.), which had partly solidified, was mixed with benzene (125 c.c.) and the precipitated *spiro*-acids (29 g.) were collected after 1 hour: the mother-liquor, mixed with light petroleum (b. p. 60–80°) and kept for 1 week, usually deposited a further quantity of the *spiro*-acids (6 g.).

The mixture of acids, m. p. usually 215–220°, was very difficult to separate into its constituents. The best results were obtained by dissolving the mixture in a large excess of acetone and carefully adding water. A small first crop (A) separated in nodules, m. p. 250–253°; the second crop (B) separated in pearly laminæ, m. p. 243°. The later crops were mixtures (m. p. 225–230°).

*trans-spiro-Acid (A) (VIII).* The first crop (A) was amorphous and separated in nodules from most of the solvents in which it was soluble; from a solution in 5% hydrochloric acid at 240°, however, the acid separated, on cooling, in lustrous fern-like forms. After crystallisation from aqueous acetone, *trans-decalin-β-spiro-cyclopropane-trans-1:2-dicarboxylic acid* melted at 264° (Found: C, 66.6; H, 8.0; equiv., 126.  $C_{14}H_{20}O_4$  requires C, 66.7; H, 7.9%; equiv., 126).

The *dianilide* crystallised from ethyl alcohol, in which it was very sparingly soluble, in soft colourless needles, m. p. 307° (decomp.) (Found: C, 77.2; H, 7.7.  $C_{26}H_{30}O_2N_2$  requires C, 77.6; H, 7.5%).

*trans-spiro-Acid (B) (IX).* The second crop (B, above) crystallised from aqueous acetone in lustrous ferns, m. p. 250° (Found: C, 66.5; H, 7.9%; equiv., 126). The *trans-spiro-acid (B)* is more soluble in solvents than its stereoisomeride (A) and melts at 220–225° when mixed with it.

The *dianilide*, m. p. 303° (Found: C, 77.4; H, 7.6%), resembled the isomeride (A) in its solubility in alcohol and in its crystalline form and melted at 280° when mixed with it.

Both the *trans-spiro*-acids are insoluble in water, benzene, and chloroform, sparingly soluble in xylene, and moderately easily soluble in acetone, ethyl acetate, and glacial acetic acid. They are



converted into the same *cis*-A-anhydride (see below) on distillation. They are, however, unchanged on melting.

The benzene-light petroleum mother-liquor from which the *trans*-*spiro*-acids had been removed (see p. 1176) was evaporated and the residue, since it showed no tendency to solidify, was esterified with ethyl alcohol and sulphuric acid in the usual way. The ethyl esters produced were twice fractionally distilled; in addition to small quantities of low-boiling esters, the following fractions were then isolated: (1) 200°/7 mm., (2) 214—215°/7 mm., (3) 224°/7 mm.

*Fraction (1).* This was boiled with concentrated hydrochloric acid for 11 hours, the residue obtained by evaporation of the acid was dissolved in benzene-light petroleum, and after several days the *cis*-*spiro*-acid (A) (VI) which had been deposited (less than 2 g.) was collected; m. p. 183—184°. The rest of the oil could not be induced to solidify.

The same acid was also prepared (a) by boiling *trans*-*spiro*-acid (A) or (B) and decomposing the anhydride thus produced, (b) from the above mixture of *spiro*-acids, m. p. 180—240°, which could not be separated by fractional crystallisation. This mixture was heated as rapidly as possible until it melted and was then boiled at the ordinary pressure for a few minutes. The unchanged acid was removed with sodium carbonate, and the anhydride distilled under reduced pressure. It boiled at 212—225°/14 mm. and the viscous distillate, after being kept in contact with light petroleum (b. p. 40—60°) for several days, deposited needles which on decomposition with alkali gave the *cis*-*spiro*-acid (A), m. p. 183—184°.

Being sparingly soluble in benzene, the *cis*-*spiro*-acid (A) is best crystallised from chloroform-light petroleum (b. p. 60—80°), from which it separates in lustrous prisms, m. p. 185—186° (efferv. and formation of anhydride) (Found: C, 66.7; H, 8.0%; equiv., 131).

The *anhydride* (X), prepared by melting the *cis*-acid or by treating it with acetyl chloride, or by any of the other methods described above, crystallised from light petroleum (b. p. 60—80°) in long silky needles, m. p. 107° (Found: C, 71.8; H, 7.5.  $C_{14}H_{18}O_3$  requires C, 71.8; H, 7.7%).

*Fraction (2).* The ester was boiled with excess of hydrochloric acid, glacial acetic acid being added until it dissolved: the hydrolysis was complete in 4 hours. The lactone, isolated in the usual way, was kept in a vacuum for several days and then dissolved in benzene-light petroleum (b. p. 60—80°); after 10 weeks, the crystals (m. p. 110°) which had separated were found on recrystallisation to be identical with lactone (C), m. p. 165—166°.

*Fraction (3).* The lactone which was obtained by the hydrolysis

of this ester was found, on purification, to be identical with lactone (A), m. p.  $156^{\circ}$ .

*Hydrolysis of the Acid Product of Monobromination by Concentrated Potassium Hydroxide Solution at  $150^{\circ}$ .*—The acid monobromomonoester (120 g.) was treated with a boiling solution of potassium hydroxide (360 g.) at  $150^{\circ}$  in the same way as the neutral bromomonoester, but in this case the reaction was very vigorous. The acids were isolated in the usual way, dried (83 g.), and mixed with benzene (150 c.c.). From the mixture of *spiro*-acids (27 g.) obtained, only the *trans*-*spiro*-acid (A), m. p.  $264^{\circ}$ , could be separated by crystallisation from aqueous acetone.

The acids soluble in benzene were esterified and the following fractions were collected: (1)  $232^{\circ}/19$  mm., (2)  $240^{\circ}/19$  mm., (3)  $246-248^{\circ}/19$  mm.

*Fraction* (1) (35 g.) was hydrolysed with hydrochloric acid, and the product treated with benzene-light petroleum (b. p.  $60-80^{\circ}$ ); a small quantity of the *cis*-*spiro*-acid, m. p.  $185-186^{\circ}$ , was obtained after several weeks.

*Fraction* (2) (8 g.) gave the lactone (C), m. p.  $165-166^{\circ}$ , when hydrolysed.

*Fraction* (3) (25 g.) gave a mixture of lactones (C) and (D).

#### *Dibromination of trans-Decalin-2:2-diacetic Acid.*

The reaction which started when *trans*-decalin-2:2-diacetic acid (200 g.) was mixed with phosphorus pentachloride (400 g.) was completed by gentle heating on the steam-bath for 4–5 hours. Dry bromine (88 c.c., 2.2 mols.) was then added to the mixture, which was kept at  $50-60^{\circ}$  during 8 hours. After 20 hours, when the evolution of hydrogen bromide had ceased, the mixture was cooled, poured into absolute ethyl alcohol (1300 c.c.) at  $0^{\circ}$ , and, when the vigour of the reaction had abated, boiled for 1 hour. The whole was then freely diluted with water and the precipitated *dibromomonoester* (XXIII) was extracted with a large volume of ether, freed from the acid product by extraction with a 5% solution of sodium carbonate, dried over calcium chloride, and recovered (350 g.). The specimen for analysis was kept in a vacuum over sulphuric acid for 4 weeks (Found: Br, 32.1.  $C_{18}H_{28}O_4Br_2$  requires Br, 34.1%).

The acid fraction (above) never amounted to more than 5 g. In the earlier experiments, where the usual conditions of bromination were followed, considerable quantities of the acid monobromomonoester (V) were obtained (Found: Br, 21.6. Calc.: Br, 22.1%).

*trans-Decalin-2:2-dibromoacetic Acid* (formula as XXIII).—When the dibromo-acid chloride was poured into anhydrous formic

acid, there was a vigorous evolution of hydrogen chloride. The gummy residue obtained on evaporation of the solution was triturated with chloroform-light petroleum (b. p. 40–60°). A small quantity of a dirty white powder was obtained which, after crystallisation from the same solvent mixture, melted at 199° (decomp.) (Found: C, 40.7; H, 5.0.  $C_{14}H_{20}O_4Br_2$  requires C, 40.8; H, 4.8%).

*Hydrolysis of the Dibromo-ester (XXIII) with 64% Potassium Hydroxide Solution.*—When the dibromo-ester (110 g.) was added as rapidly as was consistent with safety to a boiling solution of potassium hydroxide (420 g.) in water (240 c.c.), it dissolved and a potassium salt separated. The solution was boiled for 5 minutes; diluted, and acidified while hot with hydrochloric acid. The precipitated heavy oil was extracted with ether (thrice), partly dried over calcium chloride, and recovered. After being kept at 90° for 2 hours and in a vacuum for 1 week, when it had become partly solid, it was mixed with benzene-light petroleum (b. p. 60–80°) (equal volumes). After 12 hours, the precipitated  $\alpha$ -keto-trans-decalin-2:2-diacetic acid (XXIV) was collected (25 g.). It crystallised from benzene in short colourless needles and from chloroform in long silky needles, m. p. 156° (Found: C, 62.7; H, 7.5; equiv., 135.  $C_{14}H_{20}O_5$  requires C, 62.7; H, 7.4%; equiv., 134).

The keto-acid decolorises alkaline permanganate slowly in the cold, but rapidly when hot. It is easily soluble in acetone and ethyl acetate. It is also soluble in hot water, from which it cannot be crystallised since it becomes hydrated and is obtained as a syrup on removal of the solvent. The *quinoxaline* derivative, prepared by heating equal quantities of the keto-acid and *o*-phenylenediamine in glacial acetic acid for 1 hour, was obtained after two crystallisations from ethyl alcohol in dirty white nodules, m. p. 230° (Found: C, 70.6; H, 7.2.  $C_{20}H_{24}O_3N_2$  requires C, 70.6; H, 7.1%).

The *semicarbazone* of the monosodium salt\* separated in rhombic plates when a mixture of the keto-acid, semicarbazide hydrochloride, and sodium acetate in concentrated aqueous solution was kept for 24 hours. The crystals, after being washed with water and alcohol, were hydrated (Found:  $H_2O$ , 3.0.  $C_{15}H_{22}O_5N_3Na \cdot 1/2H_2O$  requires  $H_2O$ , 2.6%), but became anhydrous when kept at 110°

\* It has frequently been observed that some  $\alpha$ -keto-acids fail to combine with semicarbazide (or other ketonic reagents). The reason for this abnormal behaviour probably lies in the strong acidity of these acids, which act as hydrolysing agents: one molecule forms the semicarbazone and another immediately hydrolyses it. Semicarbazones are readily formed when the carboxyl groups attached to the keto-group are neutralised.

for 3 hours. The semicarbazone then melted with frothing and decomposition at  $255^{\circ}$  (Found : Na, 6.35.  $C_{15}H_{22}O_5N_3Na$  requires Na, 6.6%).

The keto-acid does not combine with semicarbazide, phenylhydrazine, 2 : 4-dinitrophenylhydrazine, or diphenylbarbituric acid.

The *methyl* ester, prepared by boiling a solution of the keto-acid (5 g.) in methyl alcohol (40 c.c.) and concentrated sulphuric acid (4 c.c.) for 4 hours, or from the silver salt and methyl iodide, boiled at  $228^{\circ}/21$  mm. (Found : C, 64.5; H, 8.1.  $C_{16}H_{24}O_5$  requires C, 64.9; H, 8.1%). It did not give a semicarbazone, nor react with phenylhydrazine in acetic acid or alcohol. The *phenylhydrazone*, however, was obtained by heating a mixture of the keto-ester and phenylhydrazine in benzene solution on the steam-bath for 4 hours. On addition of light petroleum (b. p.  $60-80^{\circ}$ ) to the cooled product, thick plates were obtained. The phenylhydrazone is sparingly soluble in alcohol and benzene, moderately easily soluble in chloroform, and crystallises from dilute acetic acid in long, colourless, rectangular prisms, which are pale yellow in bulk; m. p.  $235^{\circ}$  (decomp.) (Found : C, 68.3; H, 7.6.  $C_{22}H_{30}O_4N_2$  requires C, 68.4; H, 7.8%). After 1 g. of the keto-acid had been boiled with 20 c.c. of 64% potassium hydroxide solution for 4 hours, 0.9 g. was recovered unchanged by dilution, acidification, and extraction with ether.

*Oxidation of the Keto-acid with Hydrogen Peroxide.*—A solution of the keto-acid in sodium carbonate was warmed during 3 hours, with frequent additions of hydrogen peroxide. Acidification then produced a crystalline precipitate which, after purification, was identified as 2-carboxy-*trans*-decahydronaphthalene-2-acetic acid (A), m. p.  $197^{\circ}$ , by comparison with a genuine specimen (J., 1929, 1959).

On distillation under reduced pressure, the keto-acid loses carbon monoxide and gives an oily substance, which is probably a mixture of the anhydrides of 2-carboxy-*trans*-decahydronaphthalene-2-acetic acids (A) and (B).

$\Delta^{2or 1}$ -*trans-Octahydronaphthalene-2-acetic Acid* (XXV).—The benzene solution from which the keto-acid had been removed (p. 1179) was evaporated and the residue, which showed no signs of crystallising after several months, was esterified with methyl alcohol (500 c.c.) and concentrated sulphuric acid (50 c.c.). After two fractional distillations of the product, various fractions, b. p.  $170-220^{\circ}/15$  mm., were obtained in addition to a fraction, b. p.  $154^{\circ}/15$  mm. (1.7 g.). This fraction was mixed with 40 c.c. of cold 10% aqueous potassium hydroxide, and enough alcohol added to form a clear solution. After 4 days, the oil precipitated on acidifica-

ation was extracted with ether, dried, and recovered and the mixture of oil and solid obtained was drained. The solid, which separated from light petroleum (b. p. 60—80°) in rhombic plates, m. p. 100—101°, was identified as  $\Delta^{2(\text{or } 1)}$ -*trans-octahydronaphthalene-2-acetic acid* by analysis (Found: C, 73.9; H, 9.4.  $\text{C}_{12}\text{H}_{18}\text{O}_2$  requires C, 74.2; H, 9.3%), and by comparison with a genuine specimen (see later). The dibromide, m. p. 183°, was identical with the dibromide of the above-mentioned acid.

The other fractions were hydrolysed with concentrated hydrochloric acid. From the resulting acids, after standing in benzene solution for 14—18 months, small quantities of the keto-acid were isolated; the remainder did not solidify and decomposed on distillation.

The aqueous solution from which the above acids had been removed by extraction with ether was evaporated to dryness. From the residue, ether extracted a mixture of oil and solid; the latter crystallised from water in prisms, m. p. 102° (not depressed by admixture with crystalline oxalic acid), and gave the usual reactions of oxalic acid.

*Hydrolysis of the Dibromo-ester (XXIII) with Methyl-alcoholic Potash.*—The dibromo-ester (100 g.) was added as quickly as possible to a boiling solution of potassium hydroxide (200 g.) in methyl alcohol (600 c.c.). The solution was boiled for 20 minutes and then evaporated to dryness. The residue was dissolved in water and acidified, and the precipitated oil extracted with ether. The residue after removal of the dried ether was kept at 100° in a vacuum for 2 hours; it then partly solidified. It was mixed with a small quantity of benzene, and the resulting *trans-decalin- $\beta$ -spiro-trans-1-methoxycyclopropane-1:2-dicarboxylic acid* (XXIX) collected; crystallised once from ethyl acetate and once from aqueous acetone, this separated in clusters of fine silky needles, m. p. 213° (Found: C, 63.7; H, 8.0; equiv., 141.  $\text{C}_{15}\text{H}_{22}\text{O}_5$  requires C, 63.8; H, 7.8%; equiv., 141). When the *trans-methoxy-spiro-acid* was boiled with hydrobromic acid ( $d$  1.45; 30 c.c.) for 4 hours, it was converted into the keto-acid (XXIV), m. p. 156° after crystallisation from chloroform.

The low-melting acid, together with the liquid acids obtained by evaporation of the benzene solution, was refluxed with acetyl chloride, the excess of which was then removed. The residue was dissolved in a large volume of ether, and the unchanged acid removed by a dilute solution of sodium bicarbonate. The anhydride distilled at 210—220°/12 mm. It was decomposed with sodium hydroxide and the liquid acid precipitated on acidification of the alkaline solution was triturated with methyl alcohol; it then partly

solidified. The solid was freed from the oil by draining on porous earthenware and crystallised from aqueous acetone. The resulting solid (m. p. 190—193°) was reconverted into the anhydride by melting, the unchanged acid being removed by sodium carbonate. After three crystallisations from light petroleum (b. p. 60—80°), the *anhydride* (XXX) separated in long, colourless, flattened needles, m. p. 145° (Found: C, 68.2; H, 7.5.  $C_{15}H_{20}O_4$  requires C, 68.2; H, 7.5%).

The *cis-methoxy-spiro-acid* (A), which was obtained by decomposing the anhydride, crystallised from aqueous acetone in short colourless needles, m. p. 204° (Found: C, 63.7; H, 7.8; equiv., 143). Mixed with the *trans-methoxy-spiro-acid* (B), it melted at 190—194°.

The substances so far described have a great tendency to retain ether, with the result that when they are placed in a vacuum they swell up, filling the whole of the desiccator, leading to considerable loss of material. This difficulty has been overcome by keeping them at 90° or 100° in a vacuum; all the ether is then completely removed. Even if they solidify in the desiccator, the lactonic acids become oils when exposed to the atmosphere or treated with sodium-dried solvents. The only method of getting them as crystalline solids has been to dissolve them in benzene—light petroleum (b. p. 60—80°) and allow the solution to stand during several months; even so, only a fraction of the material is obtained crystalline.

*Synthesis of trans-Decahydronaphthylidene-2-acetic and*  
 $\Delta^{2(\text{or } 1)}\text{-trans-Octahydronaphthalene-2-acetic Acids.}$

*Condensation of trans- $\beta$ -Decalone with Ethyl Bromoacetate: Ethyl 2-Hydroxy-trans-decalin-2-acetate (XXXI).—*Zinc (75 g.) was added to a mixture of *trans- $\beta$ -decalone* (152 g.) and ethyl bromoacetate (106 g.) in dry benzene (375 c.c.). The reaction which started after 2 hours' heating on the steam-bath was allowed to proceed without the application of heat and was then completed by heating again for  $\frac{1}{2}$  hour. The zinc compound having been decomposed with ice and dilute sulphuric acid, the benzene layer was separated, washed successively with dilute sulphuric acid, 10% sodium hydroxide solution, and water, and dried over calcium chloride. On distillation under reduced pressure, after removal of benzene, the main fraction boiled at 184°/26 mm., small quantities of esters boiling at lower and higher temperatures being also obtained. On redistillation, pure *ethyl 2-hydroxy-trans-decalin-2-acetate* boiled at 179—180°/20 mm. (Found: C, 70.0; H, 10.0.  $C_{14}H_{24}O_3$  requires C, 69.9; H, 10.1%); it had  $d_4^{25}$  1.045,  $n_D^{25}$  1.4832, whence  $[R_L]_D$  65.54 (calc., 65.63).

The hydroxy-ester was hydrolysed by boiling with 50% potassium hydroxide solution for a few minutes; the oily acid obtained on acidification partly solidified after a few hours. The solid was isolated by filtration and draining on porous earthenware. *2-Hydroxy-trans-decalin-2-acetic acid* (XXXII) is readily soluble in hot water (from which it separates in long needles) and alcohol, but is best crystallised from benzene; m. p.  $102^{\circ}$  (Found: C, 67.7; H, 9.9; equiv., 211.7.  $C_{12}H_{20}O_3$  requires C, 67.9; H, 9.5%; equiv., 212). The oil, which probably consisted of the stereoisomeride and would not solidify, was used for the preparation of the  $\alpha\beta$ -acid.

*Dehydration of the Hydroxy-acid: trans-Decahydronaphthylidene-2-acetic Acid* (XXXIII).—The hydroxy-acid (84 g.) was dissolved in acetic anhydride (220 g.; 5 mols.) and boiled for 3 hours. The residue obtained on removal of acetic anhydride under reduced pressure was diluted with water and boiled for 2 hours (distillation in steam was extremely slow and tedious). The acid, which partly solidified on cooling, was collected and drained on porous earthenware. Crystallised from light petroleum (b. p.  $60-80^{\circ}$ ), *trans-decahydronaphthylidene-2-acetic acid* separated in long colourless prisms, m. p.  $145^{\circ}$  (Found: C, 74.3; H, 9.2; equiv., 194.  $C_{12}H_{18}O_2$  requires C, 74.2; H, 9.3%; equiv., 194).

The *dibromide*,  $C_9H_{16}>CBr\cdot CHBr\cdot CO_2H$ , was prepared by keeping a mixture of the acid and bromine in chloroform solution for 2 days. The crystals obtained by evaporation of the solvent were boiled with light petroleum (b. p.  $60-80^{\circ}$ ) to remove the small quantity of the low-melting stereoisomeride that had also been formed. The dibromide separated from benzene-light petroleum (b. p.  $60-80^{\circ}$ ) in diamond-shaped crystals, m. p.  $170^{\circ}$  (Found: Br, 45.7.  $C_{12}H_{18}O_2Br_2$  requires Br, 45.2%).

A solution of the  $\alpha\beta$ -acid in sodium carbonate was immediately oxidised by a 1% solution of potassium permanganate. The resulting ketone, which was taken up in ether, was identified as *trans- $\beta$ -decalone* by its characteristic odour and in the form of its semicarbazone, m. p. and mixed m. p.  $193^{\circ}$ .

*Dehydration of the Hydroxy-ester.*—A solution of the hydroxy-ester (100 g.) in dry benzene (100 c.c.) was mixed with phosphorus oxychloride (28 g.) and heated on the steam-bath for  $4\frac{1}{2}$  hours; evolution of hydrogen chloride had then ceased. The oil precipitated on dilution with water was extracted with ether, washed with sodium carbonate and water, dried over calcium chloride, and recovered by removal of the solvent. The  $\beta\gamma$ -ester obtained (72 g.) boiled at  $170^{\circ}/24$  mm.

Alcohol was added to a mixture of the foregoing ester (77 g.)

and a solution of potassium hydroxide (25 g.) in water (100 c.c.) until a clear solution was formed. After 48 hours, the alcohol having been removed, the solution was diluted with water, and any unchanged ester extracted with ether. The oily acid precipitated on acidification partly solidified after a few hours. It was collected, drained on porous earthenware, and crystallised from light petroleum (b. p. 60—80°),  $\Delta^{2(\text{or } 1)}\text{-trans-octahydronaphthalene-2-acetic acid}$  (XXV) separating in colourless rhombic plates, m. p. 100—101° (Found: C, 74.2; H, 9.5%; equiv., 193). The acid decolorised permanganate and instantly absorbed bromine in chloroform solution. The *dibromide*,  $\text{C}_9\text{H}_{15}\text{Br} > \text{CBr} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , obtained on evaporation of the solvent crystallised from chloroform—light petroleum (b. p. 60—80°) in thick plates, m. p. 183° (Found: Br, 45.3%).

*Conversion of the  $\alpha\beta$ -Acid into the  $\beta\gamma$ -Isomeride.*—The  $\alpha\beta$ -acid (m. p. 145°) was boiled with 64% potassium hydroxide solution for 1 hour. The precipitate obtained on acidification of the diluted solution crystallised from light petroleum (b. p. 60—80°) in rhombic plates, m. p. 100—101°, of the  $\beta\gamma$ -acid.

I desire to express my thanks to Professor J. F. Thorpe, C.B.E., F.R.S., for his kind interest in this investigation, and to the Chemical Society for generous grants towards its heavy cost.

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## CXLIX.—*The Essential Oil of Backhousia angustifolia.*

### *Part II. The Isolation of Naturally Occurring $\beta$ -Diketones: Angustione and Dehydroangustione.*

By CHARLES STANLEY GIBSON, ARTHUR RAMON PENFOLD, and JOHN LIONEL SIMONSEN.

DURING an investigation of the constituents of the essential oil derived from the leaves and terminal branchlets of *Backhousia angustifolia*, which grows in Queensland, Penfold (*J. Proc. Roy. Soc. New South Wales*, 1924, **57**, 300) observed that the portion of the oil which was soluble in alkali contained a substance or a mixture of substances giving crystalline derivatives with ammonia and copper carbonate. Although the boiling point of this constituent of the oil was the same for different samples of the oil, the other physical constants, more especially the refractive index, showed somewhat large variations ( $n_D$  1.5288 and 1.5130) (*loc. cit.*, p. 308). This difference was not due solely to contamination with



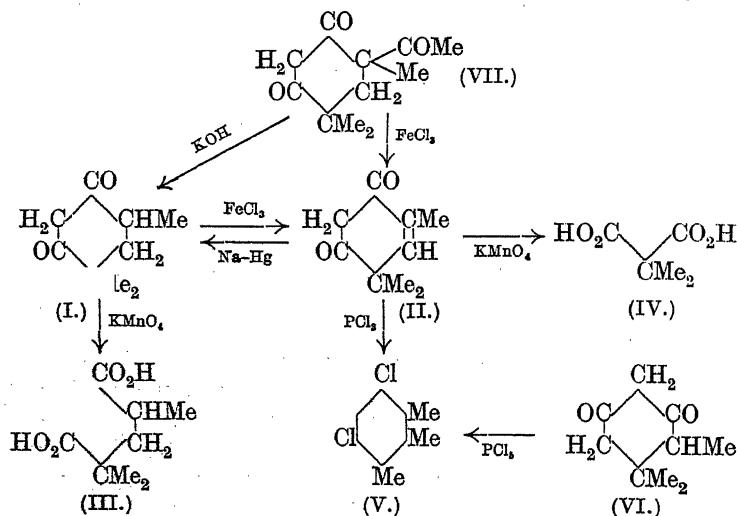
some other substance, since two individual ammonia derivatives, m. p. 135—137° and 153°, were prepared. Analyses and molecular-weight determinations appeared to indicate that the parent substances had the composition  $C_{10}H_{14}O_3$ , and this formula was provisionally adopted, although it was emphasised that evidence for the homogeneity of the substance analysed was lacking. We have now subjected the alkali-soluble fraction of this oil to a detailed investigation and have found that, depending upon conditions which remain to be determined, the substance is homogeneous and consists of either one or the other of two closely related ketones, which we have designated *angustione* and *dehydroangustione*. The constitution of the former has been rigidly established and we are able to suggest one for the latter which we regard as probably correct.

Angustione,\* identical with the substance originally analysed, has now been found to have the composition  $C_{11}H_{16}O_3$  and not  $C_{10}H_{14}O_3$  and this has been substantiated by the preparation and analysis of a number of derivatives. The most characteristic of these is formed by the action of ammonia on angustione; this substance, m. p. 130—131°, for which we suggest the name *aminoangustione*, is not an ammonium salt but has the composition  $C_{11}H_{17}O_2N$ . The formation of a substance of this composition, together with the fact that a crystalline *copper* derivative,  $C_{22}H_{30}O_6Cu$ , m. p. 192—193°, can also be prepared, suggested that angustione was a  $\beta$ -diketone (compare Haas, J., 1906, **89**, 187). The existence of this structure in angustione was supported by the preparation of a *piperonylidene* derivative and by the properties of the products formed on interaction with hydroxylamine, phenylhydrazine, and *p*-bromophenylhydrazine, whereby an *anhydro-oxime*, *anhydrophenylhydrazone*, and *anhydro-p-bromophenylhydrazone* resulted. The presence of a pyrazole ring structure in the last derivative was proved by its reduction to a pyrazoline giving the well-known Knorr reaction. With semicarbazide an *anhydro-semicarbazone* was obtained, which, for reasons to be discussed later, we consider probably differs in constitution from the anhydro-phenylhydrazones.

In the course of his preliminary experiments Penfold (*loc. cit.*, p. 311) had observed that the ketone underwent extensive degradation when oxidised with potassium permanganate. We therefore examined the action of milder reagents. On digestion with ferric chloride in acetic acid-water solution an unsaturated crystalline substance,  $C_9H_{12}O_2$ , m. p. 159—160°, was obtained, which was

\* Angustione probably occurs also in the essential oil from *Boronia thujona*, var. "A" (compare Penfold, *J. Proc. Roy. Soc. New South Wales*, 1929, **62**, 231).

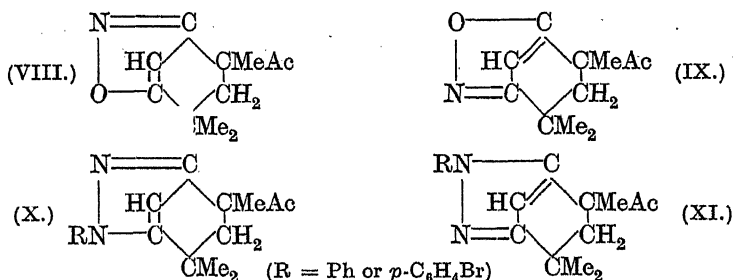
soluble in sodium bicarbonate solution and gave with ferric chloride an amethyst coloration. Oxidation of this substance with potassium permanganate gave dimethylmalonic acid, and on reduction with sodium amalgam addition of two hydrogen atoms occurred with the formation of a substance,  $C_9H_{14}O_2$ , m. p.  $130-131^\circ$ . This reduction product also gave an amethyst coloration with ferric chloride and was readily oxidised by potassium permanganate in alkaline solution, yielding  $\alpha\gamma$ -trimethylglutaric acid (III). The formation of this acid left no doubt that the substance, m. p.  $130-131^\circ$ , was the  $\beta$ -diketone, 1:1:3-trimethylcyclohexane-4:6-dione (I), and this view was confirmed by its oxidation with potassium hypobromite to the above-mentioned substituted glutaric acid. It followed from this that the substance, m. p.  $159-160^\circ$ , which can also be prepared by the oxidation of 1:1:3-trimethylcyclohexane-4:6-dione with ferric chloride, must be the corresponding unsaturated  $\beta$ -diketone, 1:1:3-trimethyl- $\Delta^2$ -cyclohexene-4:6-dione (II), which would on oxidation give dimethylmalonic acid (IV). Confirmation of this structure was obtained by the conversion of the unsaturated dione into 4:6-dichloro-1:2:3-trimethylbenzene (V) by the action of phosphorus trichloride, a reaction analogous to the preparation of this dichlorotrimethylbenzene by the action of phosphorus pentachloride on 1:1:2-trimethylcyclohexane-3:5-dione (VI) (Crossley, J., 1901, **79**, 144; Crossley and Hill, J., 1906, **89**, 881).



With the proof of the constitution of the product formed by the oxidation of angustione with ferric chloride and the indirect evidence that the saturated dione (I) was the primary product of the reaction,

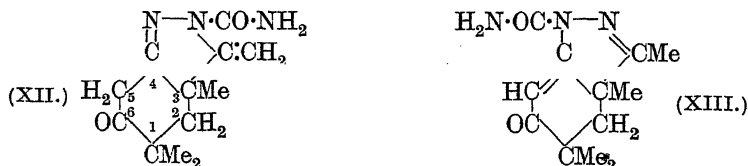
the relative positions of 9 out of the 11 carbon atoms were fixed together with those of 2 of the oxygen atoms. Although there was no direct evidence of the nature of the third oxygen, it appeared probable that the diketone contained the group  $\text{Me-CO-}$ , since if this were the case, the two remaining carbon atoms would also be accounted for. Angustione is not hydrolysed when boiled for some hours with aqueous potassium hydroxide (20%), but, when heated with an alcoholic solution of potassium hydroxide at  $150^\circ$  under pressure, it is degraded, yielding a mixture of 1:1:3-trimethylcyclohexane-4:6-dione (I) and acetic acid. This reaction proceeds very smoothly and the yield is almost quantitative; there can therefore be no doubt that angustione must be the triketone represented by (VII). Unfortunately at this stage our material was exhausted and since later distillations have given only dehydroangustione, we have been unable to examine its reactions with potassium hypobromite and potassium permanganate. It is desirable here, before proceeding to consider the constitution of dehydroangustione, to refer to the constitution of some of the derivatives of angustione mentioned above.

The product which is obtained by the action of hydroxylamine on the ketone (p. 1193) is insoluble in alkali and gives no colour with ferric chloride; it dissolves, however, in strong mineral acids and is reprecipitated on dilution. It is probably therefore either *anhydroangustione-4-oxime* (VIII) or *anhydroangustione-6-oxime* (IX).



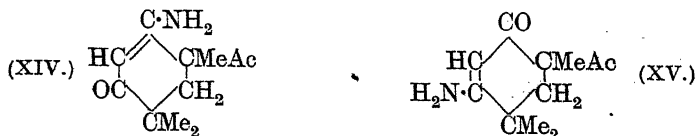
Similarly, two structures are possible for the products obtained by the action of phenylhydrazine and *p*-bromophenylhydrazine on angustione, namely, *anhydroangustione-4-phenylhydrazone* (X) or *anhydroangustione-6-phenylhydrazone* (XI). We have not attempted to determine the structure of these substances. As was mentioned above, the reaction with semicarbazide probably proceeds in a different manner. By the action of this reagent under suitable conditions (p. 1192) a substance is obtained which from its analysis is clearly an anhydro-derivative. It differs, however, very markedly in its properties from the anhydro-oxime and anhydro-phenyl-

hydrazones. Although quite colourless when powdered, the crystals show a blue fluorescence and a solution of the substance in chloroform, from which it readily separates as a gel, has a marked blue colour. It is readily soluble in alkali and gives with ferric chloride an intense indigo-blue coloration. We would suggest that this derivative is either *anhydroangustione-4-semicarbazone* (XII) or

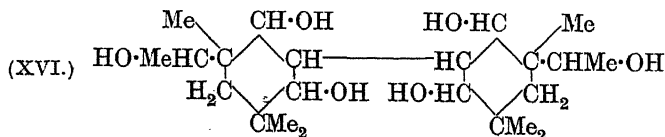


*anhydroangustione-ω-semicarbazone* (XIII): the presence of the potential enolic group in position 6 would account for the solubility in alkali and for the coloration with ferric chloride.

For aminoangustione, two formulæ (XIV) and (XV) are possible and in this case also we have no evidence which is correct.



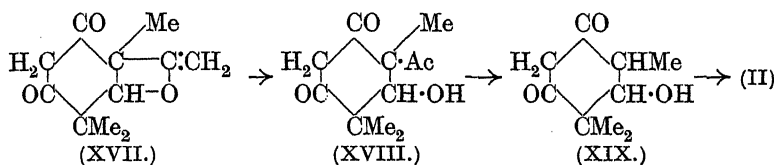
The reduction of angustione with sodium and alcohol (p. 1197) proceeds in a somewhat complex manner and we have only been able to identify two of the products: one is 1:1:3-trimethylcyclohexane-4:6-dione (I) resulting from the hydrolysis of the ketone, and the other, the main product of the reduction, is a bimolecular alcohol,  $\text{C}_{22}\text{H}_{42}\text{O}_6$ , probably (XVI).



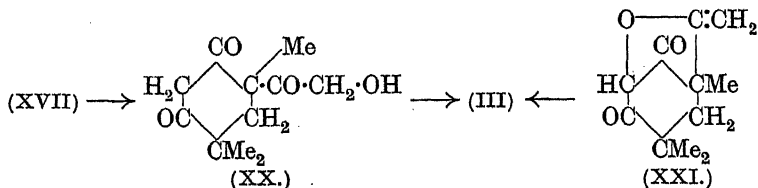
With aluminium amalgam an amorphous pinacol,  $\text{C}_{22}\text{H}_{34}\text{O}_6$ , m. p.  $153^\circ$ , is obtained, which has not been further studied.

The ketone yielding the crystalline amino-derivative, m. p.  $151^\circ$ , was at first thought to be isomeric with angustione, but careful analyses of the ketone itself and of a large number of its derivatives have shown it to contain two hydrogens less, having the composition  $\text{C}_{11}\text{H}_{14}\text{O}_3$ . Angustione and dehydroangustione are undoubtedly very closely related. Dehydroangustione is a  $\beta$ -diketone yielding an *anhydro-oxime*, *anhydro-semicarbazone*, and *anhydro-p-bromophenylhydrazone*; further, it contains a reactive  $\text{CH}_2$ - group, since it forms

a *piperonylidene* derivative. Unlike angustione, dehydroangustione is very resistant to the action of alkali and at 150° only slight hydrolysis occurs with the formation of 1 : 1 : 3-trimethyl- $\Delta^2$ -cyclohexene-4 : 6-dione (II) : this substance is, however, obtained in excellent yield when the ketone is warmed on the water-bath with sulphuric acid (50%). Since the saturated dione (I) is not oxidised under these conditions, it is obviously not an intermediate product and it became probable, therefore, that the primary product in both reactions was a hydroxycyclohexanedione. A consideration of the various possibilities has led us to the conclusion that dehydroangustione is the  $\beta$ -oxide (XVII), in which case the degradation to 1 : 1 : 3-trimethyl- $\Delta^2$ -cyclohexene-4 : 6-dione would proceed with the intermediate formation of (XVIII) and (XIX).



When dehydroangustione is oxidised with potassium permanganate, it yields a mixture of  $\alpha\gamma$ -trimethylglutaric acid and dimethylmalonic acid, the latter being formed in greater quantity. With potassium hypobromite 1- $\alpha\gamma$ -trimethylglutaric acid is obtained together with a substance having the composition  $\text{C}_8\text{H}_{10}\text{O}_3$ . The constitution of this substance has not been determined, but it is derived apparently from 1 : 1 : 3-trimethyl- $\Delta^2$ -cyclohexene-4 : 6-dione, since preliminary experiments have shown that it can be prepared by the action of potassium hypobromite on this. The formation of  $\alpha\gamma$ -trimethylglutaric acid by the oxidation of dehydroangustione can be explained only if we assume that during the oxidation hydration occurs to some extent in the reverse direction, yielding the hydroxy-ketone (XX). We recognise that this reaction is unusual and when further material becomes available we propose to attempt to establish rigidly the constitution of dehydroangustione.



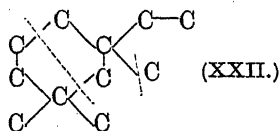
A substance having the alternative formula (XXI) would probably give a *piperonylidene* derivative and would undoubtedly yield  $\alpha\gamma$ -trimethylglutaric acid on oxidation, but its hydrolysis to the

unsaturated dione involves obvious difficulties. Furthermore it would be unlikely to yield a copper derivative.

As is the case with angustione, two formulæ are possible for all the derivatives of dehydroangustione which have been prepared. It is, however, unnecessary to consider these in detail, as we have been unable to distinguish between them. Attention may perhaps be directed to the properties of the anhydro-semicarbazone which resemble closely those of anhydroangustionesemicarbazone. It has, however, been prepared in two isomeric forms, m. p. 138—139° and 173—175° (see p. 1199). On reduction with sodium and alcohol dehydroangustione yields the same products as angustione.

Mention has been made already of the fact that angustione and dehydroangustione differ in their physical constants and this difference is shown also in their molecular refractions, that of angustione being 54.09 and of dehydroangustione 54.5. If we accept formula (VII) for angustione, the molecular refraction calculated from the Eisenlohr 1910 values (Eisenlohr, "Spectrochemie Organischen Verbindungen," p. 48) is 50.59 and the ketone therefore shows the large molecular exaltation of 3.5 units. It is difficult to find a substance of similar structure to determine how far such an exaltation is abnormal, since the *cyclohexanediones* are usually solids. A somewhat similar substance is 4-acetyl-1-methylcyclohexan-3-one, which was prepared by Léser (*Ann. Chim.*, 1902, **26**, 239). The molecular refraction of this ketone is 44.07 and the calculated value is 41.38, giving an exaltation of 2.79. Since this substance contains only two carbonyl groups, the exaltation is evidently of the same order. With dehydroangustione the molecular exaltation is even more marked, since the calculated value in this case is 49.53 if no allowance is made for the oxide ring. A high value is perhaps to be anticipated owing to the presence of the extracyclic ethylenic linkage. Any theoretical deductions from these values would be premature, but it appears justifiable to assume that a large molecular exaltation is to be expected in all *cyclohexanediones*.

In angustione and dehydroangustione we have, so far as we are aware, the first instance of the occurrence in nature of  $\beta$ -diketones. Since they contain eleven carbon atoms, they are obviously not simple derivatives of isoprene, but the formulæ which have been



assigned to them are built up from two isoprene nuclei, as will be seen by reference to the partial formula (XXII). Whether the

ketones are formed by condensation with a molecule of formaldehyde or by the degradation of a substance containing fifteen carbon atoms, we have no means of determining. It is, however, of interest to note that they contain the "ionone" ring the presence of which has recently been shown to occur in carotin (Karrer and Helfenstein, *Helv. Chim. Acta*, 1929, **12**, 1142).

Although the two ketones described in this communication are the first natural  $\beta$ -diketones to be investigated in detail, the presence of substances having similar reactions has been observed in other eucalyptus oils. Of these the most important and most readily available is leptospermol, which occurs in the oil derived from the leaves and terminal branches of *Leptospermum flavescens* (Penfold, *J. Proc. Roy. Soc. New South Wales*, 1921, **45**, 51). This ketone is at present being studied by one of us (A. R. P.) and Dr. W. F. Short and it has been found to be a  $\beta$ -diketone.

## EXPERIMENTAL.

### *Angustione.*

The ketone, which had been separated from the oil by the method described previously (*loc. cit.*, p. 308), was purified either through its amino- or copper derivative. It was regenerated from the former by gentle warming with dilute aqueous alkali (10%), the temperature not being allowed to rise above 50° and the liberated ammonia being removed under diminished pressure. The solution was acidified with dilute sulphuric acid, and the ketone isolated by extraction with ether. From the copper derivative the ketone was obtained by the decomposition of an ethereal solution with dilute sulphuric acid. When purified by either of these methods *angustione* had b. p. 129°/15 mm.,  $d_{20}^{20}$  1.089,  $n_D^{20}$  1.5137,  $[\alpha]_{5461} -5.56^\circ$ ,  $[R_L]_D$  54.09 [Found \*: (from amino-derivative) C, 67.2; H, 8.0; (from Cu derivative) C, 67.5; H, 8.1.  $C_{11}H_{16}O_3$  requires C, 67.3; H, 8.1%].

*Angustione* is a colourless viscid oil with a faint and somewhat unpleasant smell; when pure it can be kept in a loosely stoppered bottle for months without becoming discoloured. It does not yield a crystalline bromide or react with hydrogen bromide in acetic acid solution at 0°, but with hydrogen iodide it gives an unstable crystalline derivative. It was recovered unchanged after digestion with acetic anhydride, and a benzoyl derivative could not be prepared. Its alcoholic solution gives with ferric chloride an intense orange-red coloration.

*Aminoangustione* (XIV or XV).—When *angustione* in light

\* The majority of the analyses recorded in this paper are microanalyses and where two analyses are given they were made with different preparations.

petroleum solution was treated with dry ammonia, an amorphous white solid, probably an ammonium salt, separated. This was readily soluble in water and when the aqueous solution was warmed the sparingly soluble amino-derivative was precipitated. This can however, be prepared more conveniently by the method described previously (*loc. cit.*, p. 309). It is best purified by crystallisation from *cyclohexane*, in which it is somewhat sparingly soluble, and from which it separates in well-formed massive prisms, m. p. 130—131°. In absolute alcohol solution ( $c = 0.9163$ ,  $l = 4$ ),  $\alpha_{5461} = 0.31^\circ$  was observed, whence  $[\alpha]_{5461} = -8.6^\circ$  (Found : C, 68.0, 67.9; H, 8.6, 8.8; N, 7.2.  $C_{11}H_{17}O_2N$  requires C, 67.7; H, 8.7; N, 7.2%).

*Aminoangustione* is readily soluble in all the ordinary organic solvents with the exception of light petroleum, but it is very sparingly soluble in water, melting under this solvent when heated. It gives with ferric chloride the same coloration as the parent ketone. It is stable to mineral acids, but it is readily decomposed by hot alkalis with liberation of ammonia. It cannot apparently be acetylated by digestion with acetic anhydride. When it is treated in chloroform solution with bromine, a sparingly soluble oil separates, which crystallises rapidly in leaflets melting below  $0^\circ$ . This substance is probably a perbromide, since, on removal of the solvent under diminished pressure, a red gum remains from which aminoangustione can be recovered on trituration with ammonia.

The *copper* derivative of angustione was prepared most conveniently by the treatment of a light petroleum solution of the ketone with copper acetate, ammonia being added to neutralise the acetic acid liberated. The derivative, which was very readily soluble in ether and alcohol, crystallised from either benzene or dilute alcohol in blue prisms, m. p. 192—193° (Found : C, 58.5, 58.2; H, 6.5, 6.9; Cu, 14.0.  $C_{22}H_{30}O_6Cu$  requires C, 58.2; H, 6.6; Cu, 14.0%). It does not react with methyl iodide in benzene solution.

*Anhydroangustione-4(or  $\omega$ )-semicarbazone* (XII or XIII).—When a mixture of angustione (4 g.), semicarbazide hydrochloride (3.75 g.), dissolved in the minimum quantity of water, and sodium bicarbonate (2.8 g.) was kept for 3 days with occasional shaking, a viscid oil formed. The solution was cleared by the addition of alcohol and after 2 days the crystalline solid which had separated was collected; a further quantity was obtained by addition of water to the filtrate (yield, 3.2 g.). After trituration with ether, which removed a small quantity of a yellow impurity, the *semicarbazone* was recrystallised by solution in hot chloroform and addition of an equal volume of hot benzene. If allowed to cool slowly, the semicarbazone crystallised in soft serrated needles, m. p. 145° (decomp.), but if the solution was rapidly cooled, a gel was obtained: the same pheno-



menon was observed when a hot concentrated chloroform solution was rapidly cooled. The solution showed a marked blue fluorescence (Found: C, 61.6; H, 7.4.  $C_{12}H_{17}O_2N_3$  requires C, 61.3; H, 7.2%). The semicarbazone is readily soluble in water, giving a colourless solution, which on boiling clouds with the separation of an oil; it is soluble in alkali and its alcoholic solution gives with ferric chloride an intense indigo-blue coloration. In aqueous solution it reduces an ammoniacal solution of silver oxide with the formation of a silver mirror.

*Anhydroangustione-4(or 6)-phenylhydrazone* (X or XI).—This derivative was obtained in a somewhat poor yield when an alcoholic solution of the ketone was kept for some days with an excess of phenylhydrazine acetate. It crystallised from alcohol, in which it was readily soluble, in small plates, m. p. 119–120° (Found: C, 76.0; H, 7.4.  $C_{17}H_{20}ON_2$  requires C, 76.1; H, 7.5%).

*Anhydroangustione-4(or 6)-p-bromophenylhydrazone* (X or XI) crystallised from alcohol, in which it was somewhat sparingly soluble, in faintly brown prisms, m. p. 191° (Found: C, 58.5; H, 5.3; Br, 23.1.  $C_{17}H_{19}ON_2Br$  requires C, 58.8; H, 5.5; Br, 23.0%). The *p*-bromophenylhydrazone was insoluble in alkali and gave no colour with ferric chloride in alcoholic solution. When it was reduced with sodium and alcohol, a substance was obtained which gave Knorr's pyrazoline reaction.

*Anhydroangustione-4(or 6)-oxime* (VIII or IX).—A mixture of angustione (9 g.), hydroxylamine hydrochloride (3.5 g.), and sodium acetate (4.1 g.) in alcohol (35 c.c.) was heated on the water-bath for 2 hours. After about 15 minutes a blue colour developed which disappeared on further heating. The reaction mixture was distilled in steam, the volatile oil extracted with ether, the ether dried and evaporated, and the residual oil distilled under diminished pressure (22 mm.): the whole boiled at 150–152°. The colourless viscid oil, which had a strong basic smell, partly crystallised on keeping. The solid was collected, drained on porous porcelain, and recrystallised from dilute methyl alcohol; it was then obtained in needles melting not quite sharply at 41–43° (Found: C, 68.0; H, 7.6.  $C_{11}H_{15}O_2N$  requires C, 68.4; H, 7.8%). The *anhydro-oxime* was insoluble in alkali but readily soluble in concentrated hydrochloric acid, being reprecipitated on dilution. It did not give a crystalline picrate or chloroplatinate.

*Piperonylideneangustione*.—To a mixture of equimolecular proportions of angustione and piperonal dissolved in alcohol, piperidine (one drop) was added, and the solution heated to boiling. After some days a yellow crystalline solid had been deposited; it crystallised from alcohol, in which it was very sparingly soluble, in bright

sulphur-yellow, soft needles, m. p. 166—167° (Found: C, 69.6; H, 5.9.  $C_{13}H_{20}O_5$  requires C, 69.5; H, 6.0%).

*Oxidation of Angustione.*—(A) *With ferric chloride.* 1:1:3-*Trimethyl- $\Delta^2$ -cyclohexene-4:6-dione* (II). A mixture of the ketone (15 g.), ferric chloride (40 g.), acetic acid (60 c.c.), and water (130 c.c.) was boiled for 8 hours and, after remaining over-night, distilled in steam until the aqueous distillate no longer deposited a solid on saturation with ammonium sulphate. A red resinous solid remained in the distillation flask. The distillate, after saturation with ammonium sulphate, was extracted with ether, the extract dried over sodium sulphate, and the solvent evaporated; the residual red oil was warmed under diminished pressure until free from acetic acid and the crystalline solid which separated was mixed with light petroleum (b. p. 40—60°) and collected. The filtrate on distillation under diminished pressure (11 mm.) boiled at 125—135° and gave an oil from which, on cooling, a further quantity of solid could be obtained, but which consisted mainly of unchanged angustione.

1:1:3-*Trimethyl- $\Delta^2$ -cyclohexene-4:6-dione* crystallised from dilute alcohol in long needles or from light petroleum-benzene in soft needles, m. p. 159—160° (Found: C, 71.0; H, 7.8.  $C_9H_{12}O_2$  requires C, 71.1; H, 7.9%). It was readily soluble in the ordinary organic solvents with the exception of ether, in which it was somewhat sparingly soluble, and of light petroleum, in which it was very sparingly soluble. It was somewhat soluble in hot water and the solution gave with ferric chloride an amethyst coloration. It was not readily attacked by concentrated sulphuric acid and could be heated with this reagent to 110° without marked discoloration. In chloroform solution the dione rapidly absorbed bromine with the liberation of hydrogen bromide and on evaporation of the solvent 5-bromo-1:1:3-trimethyl- $\Delta^2$ -cyclohexene-4:6-dione remained, which crystallised from dilute alcohol in iridescent prisms, m. p. 126—127° (Found: C, 46.9; H, 4.8; Br, 34.3.  $C_9H_{11}O_2Br$  requires C, 46.7; H, 4.7; Br, 34.6%).

When the dione was warmed with phosphorus trichloride, evolution of hydrogen chloride occurred, and a pasty solid separated on cooling. This was dissolved in benzene, and the solution decanted from phosphorous acid, washed with alkali, and evaporated. The residual solid crystallised from dilute acetone in glistening leaflets, m. p. 77—78° (Crossley and Hills, *loc. cit.*, give 76.5°), and was evidently 4:6-dichloro-1:2:3-trimethylbenzene (V) (Found: C, 57.3; H, 5.4. Calc.: C, 57.1; H, 5.3%).

When an alcoholic solution of equimolecular proportions of the dione and piperonal was treated with a drop of piperidine and

warmed for a few minutes, a crystalline solid was obtained. This separated from alcohol in prisms, decomp.  $208-210^{\circ}$ . Although the substance itself was quite colourless, it dissolved in hot alcohol to yield a bright yellow solution, the colour disappearing on cooling. The constitution of this substance was not determined, but it consists apparently of two molecules of the dione combined with one of piperonal and analysis indicates that it is a reduction product (compare p. 1196) (Found: C, 70.9; H, 7.5.  $C_{26}H_{32}O_6$  requires C, 70.9; H, 7.3%).

(B) *With potassium ferricyanide.* A mixture of the ketone (13 g.), potassium ferricyanide (176 g.), water (400 c.c.), and potassium hydroxide solution (10%; 600 c.c.) was gently boiled for 3 hours. The cooled solution was acidified, saturated with ammonium sulphate, and extracted with ether. After removal of the solvent the residual oil was distilled in steam; a crystalline solid passed over, leaving a red resinous residue (3.7 g.). The distillate, after saturation with ammonium sulphate, was extracted with ether, and the extract dried and evaporated. The residue, which crystallised, was drained on porous porcelain to remove some adhering oil and recrystallised from dilute alcohol; it was then obtained in soft needles which were apparently homogeneous and melted sharply at  $141^{\circ}$ . Specimens from two distinct preparations were analysed and showed the substance to be a mixture of 1:1:3-trimethylcyclohexane-4:6-dione and 1:1:3-trimethyl- $\Delta^2$ -cyclohexene-4:6-dione (Found: C, 70.4, 70.5; H, 8.4, 8.7%). This was confirmed by bromination of the mixture, the bromide, m. p.  $126-127^{\circ}$  (p. 1194), being readily obtained, and by reduction with sodium amalgam, whereby it was converted quantitatively into the saturated dione, m. p.  $130-131^{\circ}$  (compare p. 1196). The 1:1:3-trimethylcyclohexane-4:6-dione present in the mixture was optically active; in alcoholic solution,  $c = 5.453$ ,  $l = 2$ ,  $\alpha_{5461} + 0.12^{\circ}$ ,  $[\alpha]_{5461} + 1.04^{\circ}$ .

*Oxidation of 1:1:3-Trimethyl- $\Delta^2$ -cyclohexene-4:6-dione.*—The dione (2 g.), dissolved in sodium carbonate solution, was oxidised with potassium permanganate (2.5%) at  $0^{\circ}$ , a current of carbon dioxide being passed through the solution. On completion of the oxidation (250 c.c.  $KMnO_4$ ) the manganese dioxide sludge was separated, and the liquid evaporated to a small bulk in a current of carbon dioxide. The acidified solution was repeatedly extracted with ether, the solvent dried and evaporated, and the residue, which immediately solidified, crystallised from hot water; it separated in glistening tablets, decomp.  $185-186^{\circ}$ . This decomposition point was not depressed on admixture with an authentic specimen of dimethylmalonic acid (Found: C, 45.7; H, 5.8. Calc.: C, 45.4; H, 6.1%).

*Reduction of 1:1:3-Trimethyl- $\Delta^2$ -cyclohexene-4:6-dione.* 1:1:3-Trimethylcyclohexane-4:6-dione (I).—The unsaturated dione (0.5 g.), dissolved in sodium carbonate solution, was reduced with sodium amalgam (2.5%; 80 g.), a current of carbon dioxide being passed through the solution during the reaction. After completion the aqueous solution was concentrated and acidified with dilute sulphuric acid and the solid (0.35 g.) which separated was collected and recrystallised from light petroleum (b. p. 60–80°); it was then obtained in glistening prisms, m. p. 130–131° (Found: C, 70.2; H, 8.9.  $C_9H_{14}O_2$  requires C, 70.1; H, 9.1%). 1:1:3-Trimethylcyclohexane-4:6-dione is readily soluble in all the ordinary organic solvents with the exception of light petroleum; it is somewhat sparingly soluble in water and its solution gives with ferric chloride an amethyst coloration. In chloroform solution it readily absorbs bromine with evolution of hydrogen bromide and on removal of the solvent a gum remains which cannot be induced to crystallise.

With piperonal the saturated dione reacts in an exactly analogous manner to the unsaturated dione (p. 1195) to yield a substance crystallising from alcohol in soft glistening prisms, m. p. 192–193°. Its solution in hot alcohol is bright yellow, although the substance itself is colourless. Analysis appears to show that it is formed by the interaction of two molecules of the dione with one of piperonal with loss of water and addition of four atoms of hydrogen (Found: C, 70.6; H, 8.3.  $C_{26}H_{36}O_6$  requires C, 70.3; H, 8.1%).

*Oxidation of 1:1:3-Trimethylcyclohexane-4:6-dione.*—(A) *With ferric chloride.* A mixture of the dione (1 g.), ferric chloride (4 g.), water (15 c.c.), and acetic acid (3 c.c.) was boiled for 4 hours and then distilled in steam; an oil passed over, which crystallised, and a red resin remained in the distillation flask. After saturation of the distillate with ammonium sulphate the solid which separated was collected and recrystallised from dilute alcohol, forming needles, m. p. 158–159°. It was identified as 1:1:3-trimethyl- $\Delta^2$ -cyclohexene-4:6-dione by the method of mixed melting point and by the preparation of the bromide, m. p. 126–127°.

(B) *With potassium permanganate.* The dione (4 g.), dissolved in sodium carbonate solution, was treated at 0° with potassium permanganate (2.5%), a current of carbon dioxide being passed through the solution during the oxidation. On completion of the reaction (370 c.c.  $KMnO_4$ ) the manganese dioxide sludge was removed, and the filtrate evaporated to a small bulk, acidified, and extracted with ether. On removal of the solvent an oil was obtained which partly crystallised. The solid was separated by solution in hot light petroleum (b. p. 40–60°), in which the oil was insoluble, and it was finally crystallised from water, from which it was obtained in

leaflets, m. p. 97° (Found : C, 55.0; H, 8.1. Calc. : C, 55.1; H, 8.0%). This acid was identical (mixed m. p.) with the acid prepared by oxidation of the dione with potassium hypobromite (see below) and consisted of  $\alpha\gamma$ -trimethylglutaric acid.

(C) *With potassium hypobromite.* A solution of the dione (2 g.) in potassium hydroxide solution (10 c.c.; KOH, 1 g.) was added all at once to a potassium hypobromite solution ( $\text{Br}_2$ , 6.5 g.; KOH, 6 g.;  $\text{H}_2\text{O}$ , 30 c.c.); bromoform separated immediately and the temperature rose to about 30°. After 1 hour, the bromoform was drawn off, the excess of hypobromite removed with sulphur dioxide, and the solution concentrated, acidified, and extracted with ether. On removal of the solvent a crystalline solid (2.2 g.) remained, m. p. 95–97°. It crystallised from water in leaflets, m. p. 97° (not depressed by admixture with acid from B). The identity of this acid with  $\alpha\gamma$ -trimethylglutaric acid was confirmed by the preparation of the anhydride, needles, m. p. 95°, and the anilide, needles, m. p. 165° (Auwers and Meyer, *Ber.*, 1890, **23**, 305; Auwers, *Annalen*, 1896, **292**, 224, give 95–96° and 165° respectively). The anilide was analysed (Found : N, 5.6. Calc. : N, 5.6%).

*Action of Potassium Hydroxide on Angustione.*—A mixture of the ketone (11.7 g.), potassium hydroxide (7 g.), water (6 c.c.), and alcohol (14 c.c.) was heated at 150° in a sealed tube for 3 hours. The liquid, which contained a crystalline potassium salt in suspension, was diluted with water, the alcohol removed on the water-bath, and the cold solution acidified; a crystalline solid mixed with some oil then separated. The solid (4.1 g.) was collected and washed with light petroleum (b. p. 40–60°) to remove the oil; when recrystallised from petroleum (b. p. 60–80°), it separated in glistening prismatic needles, m. p. 131–132° (Found : C, 70.4; H, 8.8.  $\text{C}_9\text{H}_{14}\text{O}_2$  requires C, 70.1; H, 9.1%). This substance was identified as 1 : 1 : 3-trimethylcyclohexane-4 : 6-dione by the preparation of the piperonal derivative, m. p. 192–193°.

The filtrate from which the dione had been separated was extracted with ether and, after being made alkaline with sodium carbonate solution, evaporated to dryness on the water-bath. The residual salts were extracted with absolute alcohol, and the alcohol evaporated after filtration. The crystalline residue consisted essentially of sodium acetate, since on admixture with alcohol and sulphuric acid ethyl acetate was formed, whilst on the addition of silver nitrate to an aqueous solution silver acetate was precipitated. After recrystallisation from hot water the silver salt was analysed (Found : Ag, 64.9. Calc. : Ag, 64.7%).

*Reduction of Angustione with Sodium and Alcohol.*—To a solution of the ketone (20 g.) in gently boiling alcohol (300 c.c.), sodium

(30 g.) was gradually added. After all the sodium had dissolved, steam was passed through the solution; after removal of the alcohol, a very pungent-smelling oil (A) distilled. The residue in the flask consisted of a viscid oil (B), which partly solidified.

The oil (A) was dissolved in ether, dried, recovered (6 g.), and distilled under diminished pressure (12 mm.). The first fraction, a mobile pungent oil, distilled mainly at about 90°, and the remainder, which was very viscid, at 140–150°. All attempts to prepare crystalline derivatives of these substances have been unsuccessful and they have not been identified.

The residue (B) was shaken with a little ether, and the solid (4.1 g.) collected and recrystallised from ethyl acetate, in which it was somewhat sparingly soluble. The *alcohol* crystallised in soft needles, m. p. 196–197°, which were levorotatory in alcohol,  $c = 0.4467$ ,  $l = 2$ ,  $\alpha_{5461} - 0.09^\circ$ ,  $[\alpha]_{5461} - 10.23^\circ$  [Found: C, 65.3; H, 10.7;  $M$  (Rast), 406.  $C_{22}H_{42}O_6$  requires C, 65.6; H, 10.4%;  $M$ , 404].

The alkaline solution from which the alcohol had been separated was acidified; the oil deposited partly crystallised. After draining on porous porcelain, the solid was recrystallised from light petroleum (b. p. 60–80°), separating in prismatic needles, m. p. 130–131°, and was identified as 1:1:3-trimethylcyclohexane-4:6-dione (Found: C, 70.3; H, 9.1. Calc.: C, 70.1; H, 8.7%).

### *Dehydroangustione* (XVII).

*Dehydroangustione*, after purification through its copper derivative, had b. p. 126–127°/11 mm.,  $d_{20}^{20.5^\circ} 1.103$ ,  $n_D^{20.5^\circ} 1.5255$ ,  $[\alpha]_{5461} - 2.03^\circ$ ,  $[R_L]_D 54.5$  (Found: C, 67.9; H, 7.5.  $C_{11}H_{14}O_3$  requires C, 68.0; H, 7.2%). It gives in alcoholic solution with ferric chloride the same orange-red coloration as angustione. The following derivatives were prepared by methods identical with those used for the preparation of the analogous derivatives of angustione.

*Aminodehydroangustione* crystallised from cyclohexane in glistening prismatic needles or from much hot water in leaflets, m. p. 151°. It was levorotatory in alcoholic solution,  $c = 3.98$ ,  $l = 2$ ,  $\alpha_{5461} - 0.41^\circ$ ,  $[\alpha]_{5461} - 1.76^\circ$  (Found: C, 68.3, 68.2; H, 8.0, 7.8.  $C_{11}H_{15}O_2N$  requires C, 68.4; H, 7.8%).

*Aminodehydroangustione* cannot be acetylated, being recovered unchanged after prolonged digestion with acetic anhydride. When kept for some days in alcoholic solution with semicarbazide acetate, it is converted into anhydrodehydroangustionesemicarbazone.

The *copper* derivative crystallised from benzene, in which it was somewhat more soluble than the corresponding derivative of angustione, in blue needles, m. p. 188–190° (Found: 58.8, 58.5; H, 6.0, 6.0.  $C_{22}H_{26}O_6Cu$  requires C, 58.7; H, 5.8%).

*Anhydrodehydroangustione-4(or 6)-semicarbazone* was obtained in two forms. The  $\alpha$ -semicarbazone crystallised from chloroform-benzene in prismatic needles, decomp.  $138-139^{\circ}$  (Found: N, 17.7.  $C_{12}H_{15}O_2N_3$  requires N, 18.0%). When a hot concentrated solution of the  $\alpha$ -semicarbazone was rapidly cooled, a gel was obtained which crystallised on gentle warming. The solid, m. p.  $164^{\circ}$ , obtained was now very sparingly soluble in chloroform and quite colourless, no longer showing the blue fluorescence of the  $\alpha$ -semicarbazone. The  $\beta$ -semicarbazone crystallised from dilute alcohol in small prisms, decomp.  $173-175^{\circ}$  (Found: C, 57.8; H, 6.9.  $C_{12}H_{15}O_2N_3 \cdot H_2O$  \* requires C, 57.4; H, 6.8%). Both semicarbazones gave the same deep blue colour with ferric chloride.

*Anhydrodehydroangustione-4(or 6)-p-bromophenylhydrazone* crystallised from alcohol in almost colourless prisms, m. p.  $247-248^{\circ}$  (Found: C, 59.1; H, 5.0.  $C_{17}H_{17}ON_2Br$  requires C, 59.1; H, 4.9%).

*Anhydrodehydroangustione-4(or 6)-oxime*. A mixture of the ketone (2.1 g.), hydroxylamine hydrochloride (2.5 g.), and sodium hydroxide (1.5 g. in water, 5 c.c.) with sufficient alcohol to give a clear solution was kept for 3 hours and then diluted with water. The *anhydro-oxime* thus precipitated crystallised from dilute alcohol in glistening needles, m. p.  $79-80^{\circ}$ . It was dextrorotatory in alcoholic solution:  $c = 3.09$ ,  $l = 2$ ,  $\alpha_{5461} + 0.15^{\circ}$ ,  $[\alpha]_{5461} + 4.95^{\circ}$  (Found: C, 69.1; H, 7.0.  $C_{11}H_{13}O_2N$  requires C, 69.1; H, 6.8%).

*Piperonylidenedehydroangustione* separated from alcohol in yellow needles, m. p.  $169-170^{\circ}$  (Found: C, 70.0; H, 5.8.  $C_{19}H_{18}O_5$  requires C, 69.6; H, 5.5%).

*Oxidation of Dehydroangustione*.—(A) *With potassium permanganate*. A mixture of the ketone (5 c.c.) and acetone (200 c.c.) was cooled to  $0^{\circ}$ , and finely powdered potassium permanganate gradually added. After the addition of 6 g. the oxidation became very slow; water (20 c.c.) was added and a further quantity of permanganate (10 g.). After the whole had remained over-night in the ice-box, the manganese dioxide sludge was separated and thoroughly washed with boiling water and the aqueous extract was evaporated to a small bulk in a current of carbon dioxide. The acetone on evaporation left a brown liquid, which was added to the main extract. The aqueous solution was acidified and extracted with ether (10 times), the extract dried, and the solvent evaporated. The residual oil, which had a strong odour of acetic acid, slowly crystallised when kept in a vacuum over potassium hydroxide. The solid was mixed with acetyl chloride and warmed on the water-bath for 2

\* Sufficient material was not available to determine whether this addition of water was constitutional.

hours, and the excess of acetyl chloride removed. When the residual solid was triturated with ice-cold sodium bicarbonate solution, a portion dissolved. The residue,  $\alpha\gamma$ -trimethylglutaric anhydride, m. p.  $95^\circ$ , was dissolved in boiling water; on cooling,  $\alpha\gamma$ -trimethylglutaric acid crystallised in leaflets, m. p.  $97^\circ$  (Found: C, 55.3; H, 8.0. Calc.: C, 55.1; H, 8.0%).

The sodium bicarbonate solution was acidified and extracted with ether; the solid which remained after removal of the solvent crystallised from water in tablets, decomp.  $185$ – $186^\circ$ , and was identified as dimethylmalonic acid by the method of mixed melting point.

(B) *With potassium hypobromite.* Dehydroangustione (9.8 g.) in potassium hydroxide solution (40 c.c.; KOH, 3.7 g.) was added to a solution of potassium hypobromite (KOH, 17 g.;  $\text{Br}_2$ , 24 g.;  $\text{H}_2\text{O}$ , 100 c.c.); bromoform was immediately deposited with considerable rise in temperature. After 1 hour, the excess of the hypobromite was removed with sulphur dioxide and the bromoform (4–5 g.) separated. The solution was acidified, saturated with ammonium sulphate, and extracted with ether (10 times) and the ether was dried and evaporated. The residual oil was distilled in steam and the distillate, which contained a heavy oil, was saturated with ammonium sulphate and extracted with ether. The oil (5 g.) left on removal of the solvent was distilled under diminished pressure (11 mm.); it boiled at  $125$ – $130^\circ$  and partly crystallised on keeping. The solid was collected, washed with light petroleum, and recrystallised from this solvent, separating in long prismatic needles, m. p.  $88.5^\circ$  (Found: C, 62.3; H, 6.6.  $\text{C}_8\text{H}_{10}\text{O}_3$  requires C, 62.3; H, 6.5%). This substance, which, as has already been mentioned, has not been identified, gives no colour with ferric chloride in aqueous solution.

The filtrate from which the substance, m. p.  $88.5^\circ$ , had been removed did not crystallise on keeping and was found to consist essentially of unchanged dehydroangustione.

The aqueous residue from the steam distillation was made alkaline, concentrated, acidified, and extracted with ether. On evaporation of the solvent an oil was obtained which partly crystallised. On trituration with hot light petroleum the greater part dissolved, leaving a red resinous residue; evaporation of the light petroleum left colourless crystals which separated from hot water in glistening leaflets, m. p.  $91$ – $92^\circ$ . There can be no doubt that this acid was 1- $\alpha\gamma$ -trimethylglutaric acid; in water,  $c = 1.123$ ,  $l = 2$ ,  $\alpha_{5461} = 0.19^\circ$ ,  $[\alpha]_{5461} = 16.9^\circ$  (Found: C, 55.2; H, 8.0.  $\text{C}_8\text{H}_{14}\text{O}_4$  requires C, 55.1; H, 8.0%).

*Action of Potassium Hydroxide on Dehydroangustione.*—Dehydro-



angustione was heated with an alcoholic solution of potassium hydroxide under the same conditions as those used for the hydrolysis of angustione. On completion of the reaction the tube contained a sparingly soluble potassium salt which crystallised in prisms. The reaction product, which was an oil, was dissolved in light petroleum (b. p. 40–60°) and kept for some days in the ice-box; the crystalline solid (yield, 0.3 g. from 10 g.) that had separated was recrystallised from light petroleum–benzene; it separated in felted needles, m. p. 159–160°, and was identified as 1 : 1 : 3-trimethyl- $\Delta^2$ -cyclohexene-4 : 6-dione by the method of mixed melting point and by analysis (Found : C, 71.2; H, 8.0. Calc. : C, 71.1; H, 7.9%).

*Action of Sulphuric Acid on Dehydroangustione.*—A mixture of the ketone (5 c.c.), sulphuric acid (10 c.c.), and water (10 c.c.) was heated on the water-bath for 8 hours. The oil slowly dissolved and a deep red colour developed, some sulphur dioxide being liberated. The cooled solution was diluted with water and the solid which separated (3.4 g.) was recrystallised from dilute alcohol; it was obtained in needles, m. p. 159–160°, and was identified as 1 : 1 : 3-trimethyl- $\Delta^2$ -cyclohexene-4 : 6-dione. The hydrolysis can also be effected with dilute sulphuric acid (10%), but owing to the sparing solubility of the ketone the time required is very much longer.

*Reduction of Dehydroangustione.*—Dehydroangustione was reduced with sodium and alcohol in the same manner as angustione (p. 1197). The products obtained were identical, but in this case a considerable quantity of a viscid red oil was also formed. The yields of the various products from 20 g. of ketone were : dione, 2 g.; bimolecular alcohol, 3 g.; oil volatile in steam, 5 g.

We have to express our thanks to Prof. Robinson for many valuable suggestions. We are indebted to the Government Grant Committee of the Royal Society for a grant which has defrayed part of the cost of this investigation.

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### CL.—*The Effect of Gas Pressure on the Colour of Halogen Vapours.*

By ALEXANDER SHEARER and ROBERT WRIGHT.

It was recently shown (J., 1929, 1364) that the deeper colour of iodine vapour in the presence of a gas as compared with that in a vacuum was independent of the nature of the gas used, and took

place even when the iodine vapour was unsaturated. It was suggested that this "Dewar" effect might be attributed simply to the pressure of the inactive gas.

A further series of absorption spectra photographs has now been made, in which the iodine vapour was submitted to different air pressures ranging from zero to about 2 atm. The iodine was contained in a Lilburn flask, as previously described, but in the present case the flask was connected to a manometer and a compression pump. Throughout the whole series a deepening of colour was produced step by step with increase of pressure (see Fig. 1).

Bromine vapour was examined under its own vapour pressure and when mixed with air at atmospheric pressure. The presence of the air produced a very slight increase in absorption (see Fig. 2). The ultraviolet absorption spectrum of chlorine was also examined, in a tube of about 20 cm. length with quartz ends. The pressure of the chlorine was reduced to about 0.5 atm., and its absorption spectrum photographed; air was then admitted and a second photograph taken. The pressure of the air produced no change in the absorptive power of the chlorine (see Fig. 3).

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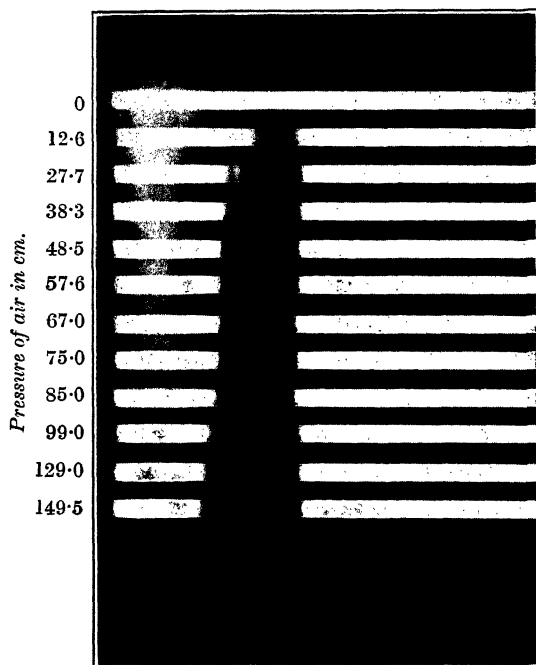
### CLI.—*The Bromination of 2-Nitro- and 2-Acetamidodiphenyl Ether.*

By HAMILTON MCCOMBIE, WILLIAM GEORGE MACMILLAN, and  
HAROLD ARCHIBALD SCARBOROUGH.

THE bromination of 2-nitrodiphenyl ether proceeded in three stages: 4-bromo-2'-nitrodiphenyl ether was formed in acetic acid solution, 2:4-dibromo-2'-nitrodiphenyl ether by the action of dry bromine in diffused light, and 2:4:4'-tribromo-2'-nitrodiphenyl ether (I) by the action of dry bromine in bright sunlight. Similarly, 2-bromo-2'-nitro-, 4-bromo-2-nitro-, and 5-bromo-2-nitro-diphenyl ethers when brominated in acetic acid solution yielded dibromo-derivatives in which the entering bromine atom occupies the 4-position in the non-nitrated nucleus. The action of dry bromine on 2:4-dibromo- and 4:4'-dibromo-2'-nitrodiphenyl ethers was to yield 2:4:4'-tribromo-2'-nitrodiphenyl ether; and 4:5'-dibromo-2'-nitrodiphenyl ether yielded 2:4:4':5'-tetrabromo-2'-nitrodiphenyl ether.

The bromination of 2-acetamidodiphenyl ether in acetic acid solution gave 5-bromo-2-acetamidodiphenyl ether as the sole product; a second bromine atom could, however, be introduced under the same conditions to give 4:5'-dibromo-2'-acetamidodiphenyl ether.

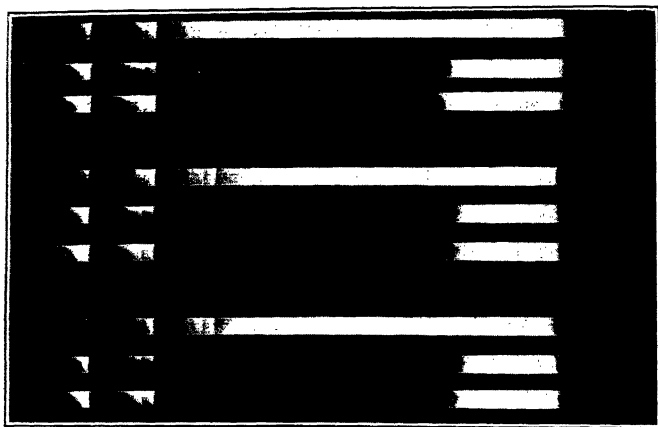
FIG. 1.



*Iodine vapour at various air pressures at 90°.*

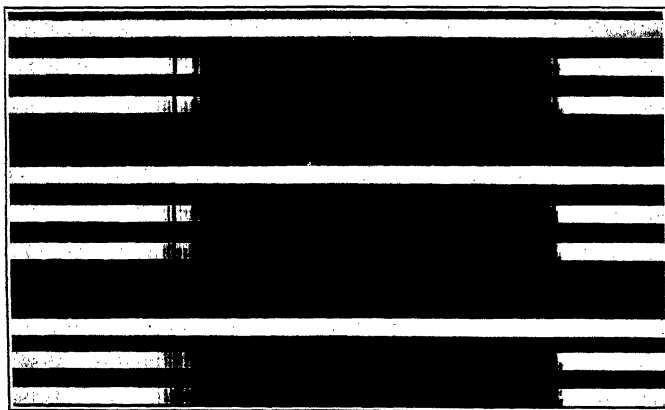
[To face page 1202.]

FIG. 2.



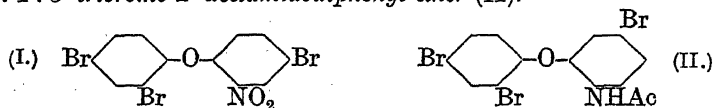
*Bromine in a vacuum and in air at 15°.*  
*Reference spectrum and three sets of exposures.*

FIG. 3.



*Chlorine in a vacuum and in air.*  
*Reference spectrum and three sets of exposures.*

The direct introduction of a third bromine atom into the molecule was not attempted. Further it was found that 2-, 4-, and 4'-bromo-2'-acetamidodiphenyl ethers were also brominated in the 5'-position; 4:4'-dibromo- and 2:4:4'-tribromo-2'-acetamidodiphenyl ethers behaved in the same manner. Under similar conditions it was found that 2:5'-dibromo-2'-acetamidodiphenyl ether was converted into 2:4:5'-tribromo-2'-acetamidodiphenyl ether (II).



The structures of the monobromo-2-nitro- and 2:4-dibromo- and 4:4'-dibromo-2'-nitrodiphenyl ethers were established by the condensation of appropriately substituted *o*-halogenonitrobenzenes with sodium or potassium halogenophenoxide. The reduction of the nitro-compound to the base and subsequent acetylation also determines the structure of the corresponding bromoacetamidodiphenyl ethers. Since both 2:4- and 4:4'-dibromo-2'-nitrodiphenyl ethers yield the same tribromo-compound, it must have the constitution 2:4:4'-tribromo-2'-nitrodiphenyl ether, and the structure of the acetamido-derivative also follows. The further bromination of 5-bromo-2-nitrodiphenyl ether, reduction and acetylation yielded a product identical with that obtained by the further bromination of 4-bromo-2'-acetamidodiphenyl ether and thus established the structure of 4:5'-dibromo-2'-nitrodiphenyl ether and of the corresponding acetamido-derivative. The orientation of the bromine atoms in 2:4:4':5'-tetrabromo-2'-nitrodiphenyl ether and of the acetyl derivative of the derived base was fixed by brominating 2:4:4'-tribromo-2'-acetamidodiphenyl ether and proving that the product was identical with that obtained by introducing three bromine atoms into the molecule of 5-bromo-2-nitrodiphenyl ether and reducing and acetylating the product.

The results show that the bromination of 2-nitro- or of a monobromo-2-nitrodiphenyl ether proceeds in stages until the 2:4-positions in the non-nitrated and the 4-position in the nitrated nucleus are substituted; a definite sequence is followed and substitution in the nitrated nucleus does not take place until the other two positions are substituted. The introduction of the third bromine atom into the 4-position in the nitrated nucleus as the sole product to be isolated was unexpected and thus in the case of both 2- and 4-nitrodiphenyl ethers there seems to be a marked steric factor which limits substitution in the positions adjacent to the oxygen linkage. A marked difference is shown between the behaviour of 2- and 4-acetamidodiphenyl ethers on bromination;

whereas 2-acetamidodiphenyl ether yielded as the sole product a compound substituted in the same nucleus as the acetamido-group, 4-acetamidodiphenyl ether yielded a single product substituted in the opposite nucleus. Further, a dibromo-derivative of 4-acetamidodiphenyl ether was obtained only with great difficulty, yet 2-acetamidodiphenyl ether yielded a dibromo-derivative with the greatest ease. The loading of the 2-acetamidodiphenyl ether molecule with bromine atoms did not appear in any way to hinder substitution in the 5-position in the same nucleus as the acetamido-group. Two factors would seem to influence the positions taken by the bromine atoms; first, the strong directive effect of the acetamido-group, which exceeds that of any other group in the molecules considered, and secondly a strong steric factor, which would almost seem to inhibit substitution in the positions ortho to the acetamido-group.

Certain substituted derivatives of 2-aminodiphenyl ether have been converted into the corresponding diphenylene oxides. It is proposed to extend the work along these lines.

#### EXPERIMENTAL.

2-Nitrodiphenyl ether was prepared by heating, at  $160^{\circ}$  for 12 hours, a mixture of 2 parts of *o*-chloronitrobenzene and 1 part of sodium phenoxide in the presence of copper powder. The product was distilled in steam to remove excess *o*-chloronitrobenzene and the residue was taken up in ether, washed with dilute soda solution and water, dried, and distilled under diminished pressure.

2-Bromo-2'-nitrodiphenyl ether was obtained when *o*-chloronitrobenzene was condensed with potassium *o*-bromophenoxide. It distilled at  $250^{\circ}/20$  mm., and separated from methyl alcohol in faintly yellow prisms, m. p.  $54^{\circ}$  (Found: Br, 27.35.  $C_{12}H_8O_3NBr$  requires Br, 27.2%).

4-Bromo-2-nitrodiphenyl ether was prepared by the condensation of 2:5-dibromonitrobenzene with potassium phenoxide. Excess 2:5-dibromonitrobenzene was removed by prolonged distillation with steam. The product was a light yellow oil, b. p.  $210^{\circ}/15$  mm. (Found: Br, 27.4.  $C_{12}H_8O_3NBr$  requires Br, 27.2%).

4-Bromo-2'-nitrodiphenyl ether was obtained when 2-nitrodiphenyl ether was treated, in carbon tetrachloride or acetic acid solution, with a slight excess of bromine as a 10% solution. The reaction was completed by warming the mixture on a water-bath for 30 minutes and then pouring it into a dilute solution of sodium sulphite. It separated from methyl alcohol in faintly yellow needles, m. p.  $72^{\circ}$  (Found: Br, 27.05.  $C_{12}H_8O_3NBr$  requires Br, 27.2%). The same

product was obtained when *o*-chloronitrobenzene was condensed with potassium *p*-bromophenoxide.

*5-Bromo-2-nitrodiphenyl Ether*.—2 : 4-Dibromonitrobenzene (1.1 mols.) was condensed with sodium phenoxide (1 mol.), in the presence of phenol and copper powder, at 150° for 18 hours. The compound, extracted in the usual manner, crystallised from methyl alcohol in yellow plates, m. p. 108° (Found : Br, 26.95.  $C_{12}H_9O_3NBr$  requires Br, 27.2%).

*2 : 4-Dibromo-2'-nitrodiphenyl ether* was obtained when 2-nitro- or 4-bromo-2'-nitrodiphenyl ether was treated with an excess of dry bromine, and the solution kept until it solidified. The product was warmed with a dilute solution of sodium sulphite and crystallised from methyl alcohol. 2 : 4-Dibromo-2'-nitrodiphenyl ether separated from light petroleum (b. p. 40—60°) in small yellow needles, m. p. 80°. The condensation of *o*-chloronitrobenzene with potassium 2 : 4-dibromophenoxide, at 200° for 24 hours, yielded the same product (Found : Br, 43.0.  $C_{12}H_7O_3NBr_2$  requires Br, 42.9%).

*4 : 4'-Dibromo-2-nitrodiphenyl ether* was prepared by treating 4-bromo-2-nitrodiphenyl ether with a slight excess of bromine in acetic acid solution. It separated from methyl alcohol in pale yellow needles, m. p. 94° (Found : Br, 42.9.  $C_{12}H_7O_3NBr_2$  requires Br, 42.9%). The same product was obtained when 2 : 5-dibromonitrobenzene was condensed with potassium *p*-bromophenoxide.

*4 : 5'-Dibromo-2'-nitrodiphenyl ether* was obtained when 5-bromo-2-nitrodiphenyl ether was treated with a slight excess of bromine in acetic acid solution. It crystallised from methyl alcohol in yellow plates, m. p. 99° (Found : Br, 42.8.  $C_{12}H_7O_3NBr_2$  requires Br, 42.9%).

*2 : 4 : 4'-Tribromo-2'-nitrodiphenyl ether* was obtained when 2-nitro-, 4-bromo-2'-nitro-, 4-bromo-2-nitro-, or 2 : 4-dibromo-2'-nitro-diphenyl ether was dissolved in dry bromine, and the solution kept in sunlight until a solid mass was formed. Excess bromine was removed with dilute aqueous sodium sulphite, and the product crystallised from acetic acid. It separated from methyl alcohol in pale yellow prisms, m. p. 102° (Found : C, 31.65; H, 1.5; Br, 53.3.  $C_{12}H_6O_3NBr_3$  requires C, 31.85; H, 1.35; Br, 53.1%).

*2 : 4 : 4' : 5'-Tetrabromo-2'-nitrodiphenyl ether* was prepared by dissolving 5-bromo-2-nitrodiphenyl ether in excess of dry bromine and keeping the solution in sunlight until a solid mass was obtained. It crystallised from ethyl alcohol or acetic acid in yellow needles, m. p. 170° (Found : Br, 59.95.  $C_{12}H_5O_3NBr_4$  requires Br, 60.2%).

*2-Acetamidodiphenyl Ether*.—2-Nitrodiphenyl ether was reduced with stannous chloride in ethereal hydrogen chloride solution by refluxing for 3 hours. The ether was removed and the base was

liberated with 30% sodium hydroxide solution, taken up in ether, and distilled under diminished pressure. 2-Aminodiphenyl ether was obtained as a light yellow oil, b. p.  $173^{\circ}/20$  mm., m. p.  $44^{\circ}$ . It was acetylated with acetic acid (4 parts) and acetic anhydride (1 part) by refluxing for 20 hours. On pouring the solution into water an oil was obtained which solidified slowly. The acetyl derivative crystallised from dilute methyl alcohol or light petroleum (b. p.  $60-80^{\circ}$ ) in prisms, m. p.  $81^{\circ}$ .

*2-Bromo-2'-acetamidodiphenyl Ether.*—2-Bromo-2'-nitrodiphenyl ether was reduced with stannous chloride in ethereal hydrogen chloride solution, and the base extracted in the usual manner. 2-Bromo-2'-aminodiphenyl ether crystallised from light petroleum (b. p.  $40-60^{\circ}$ ) in clustered needles, m. p.  $60^{\circ}$  (Found: Br, 30.3.  $C_{12}H_{10}ONBr$  requires Br, 30.3%). The base was acetylated by refluxing it for 2 days with acetic anhydride (1 part) and acetic acid (10 parts); the product crystallised from methyl alcohol or light petroleum (b. p.  $60-80^{\circ}$ ) in needles, m. p.  $95^{\circ}$  (Found: Br, 26.3.  $C_{14}H_{12}O_2NBr$  requires Br, 26.1%).

2-Bromo-2'-diacetamidodiphenyl ether was obtained when 2-bromo-2'-aminodiphenyl ether was refluxed with a mixture of acetic anhydride (1 part) and acetic acid (3 parts) for 36 hours. It separated from methyl alcohol or light petroleum in heavy prisms, m. p.  $105^{\circ}$  (Found: Br, 23.1.  $C_{16}H_{14}O_3NBr$  requires Br, 23.0%).

*4-Bromo-2-aminodiphenyl Ether.*—4-Bromo-2-nitrodiphenyl ether was reduced in the usual manner. The base distilled at  $222^{\circ}/15$  mm. and the light yellow oil slowly solidified; it separated from light petroleum in clustered needles, m. p.  $54^{\circ}$  (Found: Br, 30.3.  $C_{12}H_{10}ONBr$  requires Br, 30.3%). Acetylation of the base was attempted under various conditions, but the product was invariably a thick oil which would neither solidify nor crystallise from any of the usual solvents.

4-Bromo-2'-aminodiphenyl ether was obtained, by the reduction of 4-bromo-2'-nitrodiphenyl ether in the usual manner, as a light yellow oil, b. p.  $211^{\circ}/15$  mm. (Found: Br, 30.5.  $C_{12}H_{10}ONBr$  requires Br, 30.3%). The acetyl derivative was obtained by refluxing the base with a mixture of acetic anhydride and acetic acid; it separated from methyl alcohol in prisms, m. p.  $106^{\circ}$  (Found: Br, 25.95.  $C_{14}H_{12}O_2NBr$  requires Br, 26.1%).

*5-Bromo-2-acetamidodiphenyl Ether.*—2-Acetamidodiphenyl ether was brominated in acetic acid solution in the presence of fused sodium acetate, or 5-bromo-2-nitrodiphenyl ether was reduced and the base acetylated. The acetyl derivative separated from methyl alcohol in prisms, m. p.  $146^{\circ}$  (Found: Br, 25.95.  $C_{14}H_{12}O_2NBr$  requires Br, 26.1%).



5-Bromo-2-aminodiphenyl ether was obtained by the reduction of the nitro-compound or by refluxing the acetyl derivative with ethyl-alcoholic hydrochloric acid for 4 hours. It separated from light petroleum (b. p. 40—60°) in plates, m. p. 46° (Found: Br, 30.15.  $C_{12}H_{10}ONBr$  requires Br, 30.3%). The *hydrochloride* crystallised from a solution of the base in dilute hydrochloric acid in needles, m. p. 186° (Found: HCl, 12.15.  $C_{12}H_{10}ONBr \cdot HCl$  requires HCl, 12.15%).

2:4-Dibromo-2'-aminodiphenyl ether was prepared by reducing the corresponding nitro-compound in the usual manner and was liberated as a thick yellow oil which did not solidify. It was purified by conversion into the *hydrochloride*, which separated from dilute hydrochloric acid solution in plates, m. p. 180° (Found: HCl, 9.5.  $C_{12}H_9ONBr_2 \cdot HCl$  requires HCl, 9.6%). The base was acetylated with a mixture of acetic acid and anhydride; the *acetyl* derivative crystallised from light petroleum (b. p. 60—80°) in needles, m. p. 117° (Found: Br, 41.3.  $C_{14}H_{11}O_2NBr_2$  requires Br, 41.5%).

2:5'-Dibromo-2'-acetamidodiphenyl Ether.—2-Bromo-2'-acetamidodiphenyl ether was treated with a slight excess of bromine in acetic acid solution in the presence of fused sodium acetate. It separated from light petroleum (b. p. 80—100°) in clustered needles, m. p. 112° (Found: Br, 41.5.  $C_{14}H_{11}O_2NBr_2$  requires Br, 41.5%).

4:4'-Dibromo-2'-aminodiphenyl ether was prepared by the reduction of 4:4'-dibromo-2'-nitrodiphenyl ether and obtained as an oil, b. p. 240°/15 mm., which slowly solidified and then crystallised from methyl alcohol in needles, m. p. 70° (Found: Br, 46.5.  $C_{12}H_9ONBr_2$  requires Br, 46.65%). The *acetyl* derivative, prepared in the usual manner, separated from methyl alcohol or benzene in needles, m. p. 142° (Found: Br, 41.35.  $C_{14}H_{11}O_2NBr_2$  requires Br, 41.55%).

4:5'-Dibromo-2'-acetamidodiphenyl ether was obtained when 4:5'-dibromo-2'-nitrodiphenyl ether was reduced and the base acetylated; or when 4-bromo-2'-acetamidodiphenyl ether was brominated in acetic acid solution in the presence of fused sodium acetate. It crystallised from methyl alcohol in needles, m. p. 144° (Found: Br, 41.55.  $C_{14}H_{11}O_2NBr_2$  requires Br, 41.55%). 4:5'-Dibromo-2'-aminodiphenyl ether was prepared by refluxing the *acetyl* derivative with alcoholic hydrochloric acid for 3 hours; it separated from methyl alcohol in needles, m. p. 82° (Found: Br, 46.4.  $C_{12}H_9ONBr_2$  requires Br, 46.65%). The *hydrochloride* separated from dilute hydrochloric acid solution in needles, m. p. 202° (Found: HCl, 9.65.  $C_{12}H_9ONBr_2 \cdot HCl$  requires HCl, 9.6%).

2:4:4'-Tribromo-2'-aminodiphenyl ether, obtained by the reduc-

tion of 2:4:4'-tribromo-2'-nitrodiphenyl ether with stannous chloride in ethereal hydrogen chloride solution, separated from methyl alcohol or light petroleum in rosetted needles, m. p. 83° (Found: Br, 57.1.  $C_{12}H_8ONBr_3$  requires Br, 56.9%). It was acetylated in the usual manner and the *acetyl* derivative separated from methyl alcohol in needles, m. p. 127° (Found: Br, 51.65.  $C_{14}H_{10}O_2NBr_3$  requires Br, 51.7%).

2:4:5'-Tribromo-2'-acetamidodiphenyl ether was obtained when 2:4- or 2:5'-dibromo-2'-acetamidodiphenyl ether was treated with bromine in acetic acid solution in the presence of fused sodium acetate. It separated from methyl alcohol in needles, m. p. 147° (Found: Br, 51.7.  $C_{14}H_{10}O_2NBr_3$  requires Br, 51.7%).

4:4':5'-Tribromo-2'-acetamidodiphenyl ether was obtained from 4:4'-dibromo-2'-acetamidodiphenyl ether by bromination in the usual manner; and also from 5-bromo-2'-acetamidodiphenyl ether by bromination in acetic acid solution on the water-bath. It crystallised from methyl alcohol in needles, m. p. 167° (Found: Br, 51.6.  $C_{14}H_{10}O_2NBr_3$  requires Br, 51.7%). 4:4':5'-Tribromo-2'-aminodiphenyl ether, obtained by deacetylation in alcoholic hydrochloric acid solution, crystallised from methyl alcohol or light petroleum in needles, m. p. 120° (Found: Br, 56.7.  $C_{12}H_8ONBr_3$  requires Br, 56.85%). The *hydrochloride* of the base separated from methyl-alcoholic hydrochloric acid solution in needles, m. p. 222° (Found: HCl, 7.7.  $C_{12}H_8ONBr_3 \cdot HCl$  requires HCl, 7.9%).

2:4:4':5'-Tetrabromo-2'-acetamidodiphenyl ether was prepared by treating 2:4:4'-tribromo-2'-acetamidodiphenyl ether with excess of bromine in acetic acid solution in the presence of fused sodium acetate; after standing in the sunlight and warming to 70°, a partly brominated product was obtained, from which the unchanged tribromo-compound was separated by refluxing with light petroleum. The residue crystallised from ethyl alcohol in needles, m. p. 210° (Found: Br, 58.9.  $C_{14}H_9O_2NBr_4$  requires Br, 58.9%). The same product was obtained when 2:4:4':5'-tetrabromo-2'-nitrodiphenyl ether was reduced and the base acetylated in the usual manner.

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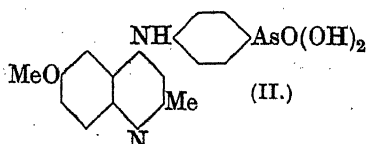
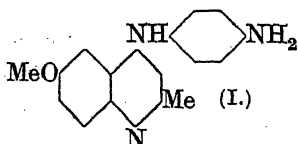
CLII.—*Quinoline Compounds containing Arsenic.*  
*Part I. Synthesis of 6-Methoxyquinoline Derivatives of Aminophenylarsinic Acids.*

By ROBERT HENRY SLATER.

THE chemotherapeutic activity in malaria of certain 6-methoxyquinoline compounds, such as quinine and plasmoquine (compare Barger and Robinson, J., 1929, 2947), and of arsenic (particularly in chronic cases where quinine has only a slight curative action) would seem to indicate that a highly efficient anti-malarial might be produced by the combination of a 6-methoxyquinoline derivative with an arsenic compound.

For the synthesis of compounds of this type, 4-chloro-6-methoxy-2-methylquinoline, easily accessible (Conrad and Limpach, *Ber.*, 1888, 21, 1651) and containing labile halogen, appeared to be a suitable initial material. The first method investigated, namely, direct condensation with *o*- or *p*-aminophenylarsinic acid, was unsuccessful, whether the two substances were heated together (a) in the dry state, (b) in presence of quinoline, or (c) in boiling amyl alcohol to which anhydrous potassium carbonate and a trace of copper powder and cuprous iodide had been added (compare Burton and Gibson, J., 1926, 459; Wintersteiner and Lieb, *Ber.*, 1928, 61, 1126).

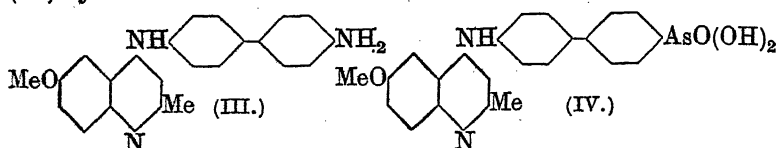
When, however, 4-chloro-6-methoxy-2-methylquinoline was heated with an excess of *p*-phenylenediamine, 4-*p*-aminoanilino-6-methoxy-2-methylquinoline (I) was produced. This base was converted into *p*-6'-methoxy-2'-methyl-4'-quinolylaminophenylarsinic acid (II) by means of the Bart reaction, uniform yields being obtained when the solid diazo-compound was employed.



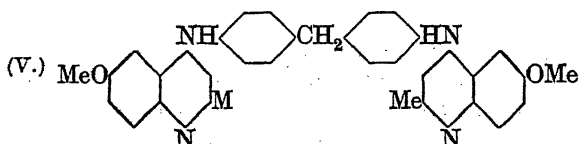
By a similar series of reactions 4-*m*-aminoanilino-6-methoxy-2-methylquinoline and *m*-6'-methoxy-2'-methyl-4'-quinolylaminophenylarsinic acid were obtained.

4-Chloro-6-methoxy-2-methylquinoline and benzidine condensed readily when heated together, with formation of 4-benzidino-6-methoxy-2-methylquinoline (III). This base was readily converted

into 4'-6''-methoxy-2''-methyl-4''-quinolyldiaminodiphenylarsinic acid (IV) by means of the Bart reaction.



*pp'*-Diaminodiphenylmethane and 4-chloro-6-methoxy-2-methylquinoline condensed slowly when heated together. *pp'*-Di-6'-methoxy-2'-methyl-4'-quinolyldiaminodiphenylmethane (V) was the only product even when a large excess of *pp'*-diaminodiphenylmethane was present.



Monoquinolyl derivatives also have not yet been obtained from *o*-tolidine or *o*-dianisidine and 4-chloro-6-methoxy-2-methylquinoline. Attempts are being made to condense these bases and various aminophenylarsinic acids with 4-bromo-6-methoxy-2-methylquinoline (which contains a more reactive halogen atom).

Several of the substances now described exhibit a remarkable tendency to form gels when warm dilute aqueous solutions of their salts are cooled, and most of them give brilliant colorations, ranging from red to purple, when they are added under suitable conditions to a dilute aqueous solution of iodine in potassium iodide. These reactions will be more fully described elsewhere.

The above quinolyldiaminodiphenylmethane and some of the intermediate compounds are being tested by the Joint Committee on Chemotherapy formed by the Medical Research Council and the Department of Scientific and Industrial Research in respect of their chemotherapeutic actions. The results of these tests will be published later.

#### EXPERIMENTAL.

4-*p*-Aminoanilino-6-methoxy-2-methylquinoline (I).—A mixture of 4-chloro-6-methoxy-2-methylquinoline (10.4 g.) and *p*-phenylenediamine (9 g.), heated at 130–140°/15 mm. during 20 minutes, became dark brown and almost completely solid. A solution of the product in the minimum amount of hot dilute hydrochloric acid (5%) was filtered, cooled, and added to twice its volume of concentrated hydrochloric acid (*d* 1.19). From the pale green, crystalline hydrochloride (13.5 g.) which separated, the free base was

liberated by aqueous ammonia. It crystallised from aqueous alcohol (50%) in large, thick, light brown, rectangular plates, melting with loss of water at 215° (Found: C, 68.5; H, 6.2.  $C_{17}H_{17}ON_3 \cdot H_2O$  requires C, 68.7; H, 6.4%). The base is soluble in ethyl alcohol, methyl alcohol, and acetic acid, but much less soluble in benzene and light petroleum. A dilute alcoholic or acetic acid solution does not give a coloration with *N*/1000-iodine. The hydrochloride separates in fine, white, prismatic needles when hydrochloric acid is added to an alcoholic solution of the base.

The *acetyl* derivative, prepared by means of boiling acetic anhydride, crystallised from aqueous alcohol (20% alcohol) in large, pale yellow rhombohedra which contained water of crystallisation. After dehydration at 150° the compound has m. p. 240° (Found: C, 71.2; H, 5.7; N, 12.8.  $C_{19}H_{19}O_2N_3$  requires C, 71.0; H, 6.0; N, 13.1%). It is soluble in alcohol and acetic acid, but practically insoluble in benzene and light petroleum. A warm dilute acetic acid solution (2%) sets to a firm jelly on cooling. A dilute acetic acid solution gives with *N*/1000-iodine a brilliant blue coloration, which disappears on warming and reappears on cooling. A dilute alcoholic solution behaves similarly, but fresh iodine solution has to be added to the cooled solution in order to restore the blue colour. A blue coloration is also produced when a dilute aqueous solution of potassium iodide is added to a mixture of an acetic acid solution of the acetyl compound and bromine water. Hydrochloric acid precipitates the hydrochloride from an alcoholic solution in yellow feathery needles which are sparingly soluble in water.

*p*-6'-Methoxy-2'-methyl-4'-quinolylaminophenylarsinic Acid (II).—A mixture of 4-*p*-aminoanilino-6-methoxy-2-methylquinoline (5.6 g.) and hydrochloric acid (9 c.c.; *d* 1.19) was cooled to -5° and diazotised (sodium nitrite, 1.6 g.; water, 7 c.c.) below 0°. After an hour, the mixture was neutralised at 0° with 5*N*-sodium hydroxide, and sodium arsenite solution (a mixture of arsenious oxide, 3 g., in 5*N*-sodium hydroxide solution, 6 c.c.; sodium carbonate, 6 g., in water, 18 c.c.; and 10% copper sulphate solution, 0.6 c.c., to which was added sufficient aqueous ammonia to give the soluble complex salt) added. The whole was kept at room temperature for 16 hours and then warmed gently on the water-bath until evolution of nitrogen ceased. After filtration, the solid residue was extracted thrice with small quantities of aqueous sodium hydroxide (5%). The hydrogen-ion concentration of the combined filtrates was adjusted with hydrochloric acid to  $p_H$  7.5; the *arsinic acid* was then quantitatively precipitated as a white gelatinous solid. This was collected and repeatedly dissolved in dilute sodium

hydroxide solution and reprecipitated at its isoelectric point ( $p_H$  7.5) with nitric acid; the stellate clusters of fine, white, prismatic needles obtained were washed with water (yield, 0.5—3.2 g.). The acid was unmelted at  $307^\circ$  (Found: N, 7.6; As, 19.4.  $C_{17}H_{17}O_4N_2As$  requires N, 7.2; As 19.3%).

A more uniform yield was obtained by the following method. A well-stirred mixture of 4-*p*-aminoanilino-6-methoxy-2-methylquinoline (5.6 g.) and glacial acetic acid (30 c.c.) was cooled to  $10^\circ$ , sodium nitrite (1.6 g.) added gradually, and the clear reddish-brown solution poured into dry ether (150 c.c.). The solid orange diazonium compound, which separated, was collected, washed with dry ether, and added to the sodium arsenite mixture (as used above). After standing over-night, the reaction product was worked up and the arsinic acid isolated as in the last experiment (yield, 2.6 g.).

The arsinic acid is practically insoluble in water and the usual organic solvents. It dissolves readily in dilute sodium and ammonium hydroxide solutions and in moderately concentrated hydrochloric acid. No satisfactory explanation can be advanced of the curious phenomenon that the acid is precipitated from a solution of its sodium salt in a crystalline form by nitric acid (*vide supra*) and, under exactly similar conditions, in a gelatinous form by hydrochloric acid. A colloidal solution of the arsinic acid in dilute acetic acid gives a purple coloration with *N*/1000-iodine.

The sodium salt is precipitated in colourless plates when concentrated sodium hydroxide solution is added to a solution of the arsinic acid in dilute alkali. The following salts are precipitable from an aqueous solution of the ammonium salt: magnesium salt, white, gelatinous, insoluble in hot water; barium salt, white, gelatinous, soluble in hot water, crystallises on cooling in fine slender needles; calcium salt, white, gelatinous, less soluble in hot water; silver salt, pale yellow, curdy, insoluble in hot water; mercuric salt, white, curdy, insoluble in hot water.

**4-*m*-Aminoanilino-6-methoxy-2-methylquinoline.**—A mixture of 4-chloro-6-methoxy-2-methylquinoline (10.4 g.) and *m*-phenylenediamine (10 g.) was heated at  $140^\circ/20$  mm. for  $1\frac{1}{2}$  hours, the almost solid product dissolved in hot dilute hydrochloric acid (5%), and the filtered solution rendered alkaline with aqueous ammonia. The base obtained crystallised from aqueous alcohol (20% alcohol) in long, pale brown, rectangular, prismatic needles (10 g.), *m. p.*  $230$ — $231^\circ$  (Found: C, 73.4; H, 6.2; N, 14.7.  $C_{17}H_{17}ON_2$  requires C, 73.1; H, 6.1; N, 15.0%).

4-*m*-Aminoanilino-6-methoxy-2-methylquinoline is readily soluble in ethyl alcohol, methyl alcohol, and acetic acid, but sparingly soluble in benzene and light petroleum. A dilute alcoholic or acetic

acid solution gives with *N*/1000-iodine a faint red coloration, which slowly deepens. The addition of hydrochloric acid to an alcoholic solution of the base gives a white gelatinous precipitate of the hydrochloride.

The *acetyl* derivative crystallises from aqueous alcohol (10% alcohol) in stout, pale yellow, prismatic needles, m. p. 269° (Found : C, 71.0; H, 6.1; N, 12.7.  $C_{19}H_{19}O_2N_3$  requires C, 71.0; H, 6.0; N, 13.1%). It is slightly soluble in ethyl alcohol and acetic acid, but practically insoluble in benzene and light petroleum. A dilute alcoholic solution gives a deep blue coloration with *N*/1000-iodine and a dilute acetic acid solution gradually gives a brilliant purple coloration; these colours disappear on warming but reappear on cooling. The addition of water to a solution of the acetyl compound in concentrated hydrochloric acid produces a white gelatinous precipitate of the hydrochloride.

*m*-6'-Methoxy-2'-methyl-4'-quinolylaminophenylarsinic Acid.—This acid was obtained from 4-*m*-aminoanilino-6-methoxy-2-methylquinoline by the Bart reaction under practically the same conditions which were used in the first method of preparation of its *p*-isomeride (base, 5.6 g.; hydrochloric acid, 15 c.c. of *d* 1.14; sodium nitrite, 1.6 g., in water, 7 c.c.), but a slightly higher temperature (0—5°) was permitted. The reaction of the alkaline filtrate was adjusted with hydrochloric acid to *p*<sub>H</sub> 5 and the *arsinic acid*, then quantitatively precipitated as a white gelatinous solid, was purified by several reprecipitations from solution in dilute aqueous sodium hydroxide at the above isoelectric point (*p*<sub>H</sub> 5), washed with water, and dried (yield, 1.5 g.). It darkened at 280° but was unmelted at 300° (Found : As, 19.5.  $C_{17}H_{17}O_4N_2As$  requires As, 19.3%).

This *arsinic acid* resembles the *p*-isomeride in solubility, but it is not precipitated in a crystalline form when nitric acid is added to an aqueous solution of its sodium salt; also, the colloidal solution in dilute acetic acid does not give a coloration with *N*/1000-iodine.

The sodium salt of the *arsinic acid* is readily precipitated as a crystalline mass when concentrated sodium hydroxide solution is added to its dilute alkali solution. The following salts are insoluble in cold water: magnesium salt, white, gelatinous, slightly soluble in hot water; calcium salt, pale yellow, gelatinous, less soluble in hot water; barium salt, white, gelatinous, soluble in hot water, gelatinous precipitate on cooling; silver salt and mercuric salt, pale yellow, curdy, insoluble in hot water.

4-Benzidino-6-methoxy-2-methylquinoline (III).—A mixture of 4-chloro-6-methoxy-2-methylquinoline (5.2 g.) and benzidine (7 g.) was heated at 160° during 15 minutes and the almost solid product was digested with excess of hot dilute hydrochloric acid (5%),

which readily converted it into an insoluble yellow hydrochloride. This was extracted several times with small quantities of boiling dilute hydrochloric acid and then warmed with sodium hydroxide solution. The base (7.2 g.) liberated crystallised from toluene in fine, pale yellow, microscopic, rectangular prisms, m. p. 245° (Found: C, 77.8; H, 6.1; N, 11.5.  $C_{23}H_{21}ON_3$  requires C, 77.7; H, 6.0; N, 11.8%).

*4-Benzidino-6-methoxy-2-methylquinoline* is soluble in acetic acid and boiling toluene, but sparingly soluble in ethyl and methyl alcohols, benzene and light petroleum. Its solution in warm dilute acetic acid sets to a gel on cooling. A dilute acetic acid solution of this base gives with *N*/1000-iodine a deep purple coloration; this disappears on warming but does not reappear on cooling.

The *acetyl* derivative crystallises from aqueous alcohol in stellate clusters of fine, yellow, rectangular, prismatic needles, m. p. 159—160° (Found: N, 9.7.  $C_{25}H_{23}O_2N_3 \cdot 2H_2O$  requires N, 9.7%). It is readily soluble in ethyl and methyl alcohols and in acetic acid, but it is only slightly soluble in benzene and practically insoluble in light petroleum. A solution in warm dilute acetic acid sets to a gel on cooling. A dilute alcoholic or acetic acid solution gives with *N*/1000-iodine a brilliant purple coloration which disappears on warming and reappears on cooling. This coloration is also produced when a dilute potassium iodide solution is added to a mixture of the acetic acid solution of the *acetyl* compound and bromine water. The addition of hydrochloric acid to an alcoholic solution of the base precipitates a crystalline hydrochloride sparingly soluble in water.

*4'-6''-Methoxy-2''-methyl-4''-quinolylaminodiphenylarsinic Acid* (IV).—A well-stirred mixture of the preceding benzidino-compound (3.5 g.), hydrochloric acid (5.7 c.c. of *d* 1.19), and water (15 c.c.) was cooled to 5°, and a saturated solution of sodium nitrite (0.8 g.) added gradually below 8°. After 1 hour, the diazo-mixture was carefully neutralised at 5° with aqueous sodium hydroxide (5*N*), and sodium arsenite solution (a mixture of arsenious oxide, 2 g., in 5*N*-sodium hydroxide solution, 4 c.c.; sodium carbonate, 4 g., in water, 12 c.c.; and 10% copper sulphate solution, 0.4 c.c., to which was added sufficient aqueous ammonia to give the soluble complex salt) added. After remaining at room temperature over-night, the mixture was warmed gently on the water-bath until evolution of nitrogen ceased. After the addition of *N*-sodium hydroxide (10 c.c.) the liquid was filtered, and the residue extracted thrice with warm dilute sodium hydroxide solution. The reaction of the combined filtrates was adjusted with hydrochloric acid in the cold to *p*<sub>H</sub> 7; the *arsinic acid* then completely precipitated was purified by several precipitations (at *p*<sub>H</sub> 7) from its solution in dilute alkali



with hydrochloric acid and obtained in pale yellow needles (radially arranged) which, when washed free from sodium chloride, were converted into a gelatinous solid (yield, 2.2 g.). The acid darkened at 290° but was unmelted at 300° (Found: As, 16.0.  $C_{23}H_{21}O_4N_2As$  requires As, 16.15%).

This arsinic acid is practically insoluble in water and in the usual organic solvents, readily soluble in dilute sodium and ammonium hydroxide solutions, but only slightly soluble in hydrochloric acid. A colloidal solution in dilute acetic acid gives with *N*/1000-iodine a dark red coloration which changes to purple on the addition of hydrochloric acid. The crystalline sodium salt is readily produced in the usual way. The magnesium, calcium, and barium salts are white and gelatinous, the silver salt is pale yellow and gelatinous, and the mercuric salt pale yellow and curdy: all are insoluble in water.

*pp'*-Di-6'-methoxy-2'-methyl-4'-quinolyldiaminodiphenylmethane (V).—*pp'*-Diaminodiphenylmethane (7.5 g.) was heated to 130°, and to the melt were added 4-chloro-6-methoxy-2-methylquinoline (5.2 g.) and a trace of finely divided copper-bronze. After 3 hours' heating, the mixture, which had almost completely solidified, was digested with hot dilute hydrochloric acid (5%) and the residual, sparingly soluble, pale yellow hydrochloride (4.5 g.) was treated with warm aqueous sodium hydroxide solution. The base thus liberated crystallised from hot alcohol in small, pale brown, rectangular, prismatic needles, m. p. 144° (decomp.) (Found: C, 77.3; H, 6.0; N, 10.2.  $C_{35}H_{32}O_2N_4$  requires C, 77.7; H, 6.0; N, 10.4%). It is soluble in ethyl alcohol and acetic acid, but only sparingly soluble in benzene and light petroleum. A dilute alcoholic or acetic acid solution gives with *N*/1000-iodine a deep purple coloration, which disappears on warming but reappears on cooling. The addition of hydrochloric acid to an alcoholic solution of the base precipitates the hydrochloride in fine, yellow, rectangular, prismatic needles.

The author desires to express his thanks to the Trustees of the Carnegie Trust for the Universities of Scotland and to the Court of the Grocers' Company for a Fellowship and a Scholarship, respectively, which have enabled this work to be carried out. He is also indebted to Dr. W. O. Kermack for his interest in the investigation.

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CLIII.—*Some Derivatives of m-Xylene.*

By ERNEST G. BOYCE, WILLIAM P. RANKINE, and ALEXANDER ROBERTSON.

*m-Xylorcinolcarboxylic Acid*.—The procedure adopted by one of us (A. R.) and Robinson (J., 1927, 2196) for the preparation of *p*-orsellinic acid has proved suitable for the preparation of *m*-xylorcinolcarboxylic acid (compare Kostanecki, *Ber.*, 1886, **19**, 2323). A mixture of *m*-xylorcinol (Robertson and Robinson, *loc. cit.*) (5 g.), potassium carbonate (10 g.), and glycerol (10 g.) was heated (oil-bath at 130°) for 5 hours in an atmosphere of carbon dioxide. Addition of 15% hydrochloric acid to the cooled reaction mixture precipitated *m*-xylorcinolcarboxylic acid (4 g.), which crystallised from dilute alcohol in colourless prismatic needles, m. p. 199–200° (decomp.) (Kostanecki, *loc. cit.*, gives m. p. 196°) (Found: C, 59.5; H, 5.7. Calc. for  $C_9H_{10}O_4$ : C, 59.4; H, 5.5%). The acid quickly decomposes in boiling water into *m*-xylorcinol and carbon dioxide. The ferric chloride reaction is green in alcohol and pure blue in water. This acid, unlike  $\beta$ -orcinolcarboxylic acid (Robertson and Stephenson, this vol., p. 313), is not esterified in boiling methyl or ethyl alcohol. If sodium bicarbonate is used in the preparation, the yield is halved.

*6-Methoxy-m-4-xylylidine*.—4-Nitro-*m*-6-xylene (1 mol.) was methylated with methyl sulphate (2 mols.) and 20% aqueous sodium hydroxide (2.5 mols.) (compare Pfaff, *Ber.*, 1883, **16**, 1136). The alkali-insoluble ether crystallised from alcohol in pale yellow needles, m. p. 56–57°. Iron powder (80 g.) was added in portions of 10 g. at intervals of 3 minutes to a boiling solution of the nitro-ether (60 g.) in alcohol (300 c.c.) and concentrated hydrochloric acid (20 c.c.), and the mixture was refluxed for 5 hours, a test then showing that reduction was complete. The filtered solution was concentrated to 100 c.c., cooled, saturated with hydrogen chloride, and kept in an ice-chest. After some hours, the hydrochloride was collected, and a further quantity was isolated from the mother-liquor by concentration to 50 c.c. and renewed saturation with hydrogen chloride. The salt crystallised in glistening prisms; total yield, 50 g. Agitation of a suspension of the salt in excess of bicarbonate solution gave the amine, m. p. 83° after crystallisation from benzene-ligroin and then from dilute alcohol (colourless needles). The *acetyl* derivative crystallised from water in needles, m. p. 160° (Found: C, 68.6; H, 7.5.  $C_{11}H_{15}O_2N$  requires C, 68.7; H, 7.4%).

*6-Methoxy-m-4-xyleneol*.—The foregoing hydrochloride (17 g.) was

dissolved in 10% sulphuric acid (200 c.c.) and crushed ice (200 g.) was added after sudden cooling and shaking to ensure the separation of small crystals. Sodium nitrite (6 g.), dissolved in water (50 c.c.), was then introduced, and the mixture stirred for 15 minutes. The filtered diazo-solution was gradually added to boiling 10% sulphuric acid (600 c.c.). On cooling, 6-methoxy-*m*-4-xylene separated in pale yellow crystals. Recrystallisation from ligroin gave the substance in colourless needles, m. p. 80° (Found: C, 70.9; H, 7.8.  $C_9H_{12}O_2$  requires C, 71.0; H, 8.0%). It is readily soluble in alcohol, ether, and benzene. The phenol does not give a ferric chloride reaction.

*2-Hydroxy-6-methoxy-3 : 5-dimethylbenzaldehyde*.—Condensation of the monomethyl ether of xylocinol and hydrogen cyanide in the presence of hydrogen chloride and zinc chloride after the method of Gattermann gave a compound which on solution in water reverted to the original ether. The aldehyde was subsequently obtained by partial methylation of *m*-xylocinylaldehyde (1 mol.) (Robertson and Robinson, *loc. cit.*) with methyl iodide (1.5 mols.) and excess of potassium carbonate in acetone under reflux on the steam-bath for 2 hours. After removal of the potassium salts the acetone was distilled under diminished pressure, and the alkali-soluble residue crystallised from dilute methyl alcohol. The aldehyde formed slender colourless needles, m. p. 52° (Found: C, 66.4; H, 6.3.  $C_{10}H_{12}O_3$  requires C, 66.7; H, 6.3%). The substance gives a dark green ferric chloride reaction almost identical with that given by *m*-xylocinylaldehyde. It is insoluble in water and readily soluble in alcohol, acetone, or ethyl acetate. Condensation of the aldehyde with  $\alpha$ -methoxyacetoveratrone (Pratt and Robinson, J., 1923, 123, 745) with hydrogen chloride in dry ethyl acetate by the method of Robinson gave 3 : 5 : 3' : 4'-tetramethoxy-6 : 8-dimethylflavylium chloride in red-brown prisms; the ferrichloride crystallised from acetic acid in elongated red-brown prisms, m. p. 177–178° (Found: C, 45.6; H, 4.3.  $C_{21}H_{23}O_5, FeCl_4$  requires C, 45.6; H, 4.2%).

*m*-Xylocinol does not condense with acetonitrile by the method of Hoesch.

We are indebted to the Chemical Society for a grant which has in part defrayed the cost of this investigation.

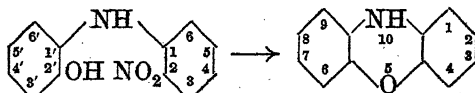
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[Received, March 25th, 1930.]

CLIV.—*The Formation of Phenoxazines.*

BY OSCAR L. BRADY and CECIL WALLER.

CERTAIN substituted 2-nitro-2'-hydroxydiphenylamines on treatment with alkali readily lose nitrous acid to give phenoxazines:



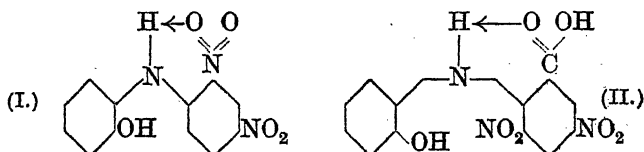
The reaction has been investigated by Turpin (J., 1891, 59, 720), Ullmann (*Annalen*, 1908, 366, 79), and Ullmann and Sané (*Ber.*, 1911, 44, 3730), but no satisfactory explanation has been suggested for the influence of other groups present in the molecule upon the reaction.

It was found by these workers that the phenoxazines are formed when the following compounds are treated with alkali: 2:4:6-trinitro-, 2:6-dinitro-, 2:4-dinitro-6-carboxy-, 2:6-dinitro-4-carboxy-, 2:6-dinitro-4-benzoyl-, 2:4-dinitro-6-sulpho-, 2:6-dinitro-4-sulpho-, 2:4-dinitro-6-methyl-, and 2:6-dinitro-4-chloro-2'-hydroxydiphenylamines. No reaction occurred, however, with 2:4-dinitro-2'-hydroxydiphenylamine. Thus in all cases where the phenoxazine was formed the 6-position was occupied, and Ullmann concluded that this was a necessary condition for the reaction to occur. In order to test this view more fully, a number of similar compounds have been investigated. In all the cases previously studied, with the exception of 2:4-dinitro-2'-hydroxy-6-methyldiphenylamine, a "negative" group occupied the 6-position. It did not seem likely that groups of such different character as NO<sub>2</sub> and CH<sub>3</sub> would activate the 2-nitro-group, but in order to test this point a group at the other end of the scale, namely, methoxyl, was tried and it was found that 2:4-dinitro-2'-hydroxy-3:6-dimethoxydiphenylamine readily gave the phenoxazine.

The presence of a methyl group in another position in the nitrated ring had no influence; 2:6-dinitro-5-methyl- and 2:6-dinitro-4-methyl-2'-hydroxydiphenylamines readily gave phenoxazines, but 2:4-dinitro-5-methyl-2'-hydroxydiphenylamine did not do so. A methyl group in the 6'-position was also without effect, 2:6-dinitro-2'-hydroxy-3:6'-dimethyldiphenylamine giving the phenoxazine and 2:4-dinitro-2'-hydroxy-6'-methyl- and 2:4-dinitro-2'-hydroxy-5:6'-dimethyl-diphenylamines failing to do so.

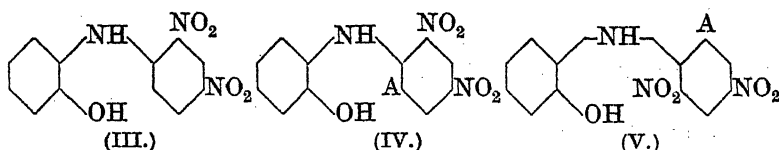
The lack of reactivity of, for example, 2:4-dinitro-2'-hydroxydiphenylamine might be due to chelation of the 2-nitro-group with

the imino-group (I) preventing its access to the hydroxyl group; the presence of another group in the 6-position which could itself



chelate (II) would negative this effect and most of the compounds investigated have such a group, but it is difficult to suppose that the methyl group would be effective in this respect. Attempts to prepare *N*-methyl derivatives in order to eliminate the possibility of chelation as in (I) were, however, unsuccessful.

The only explanation that can be suggested is a purely steric one : if the 6-position is free, for steric reasons the large nitro-group takes up a position remote from the hydroxyl group, thus bringing the



6-position near it (III). If there is a group in the 6-position, there is less reason for the compound to be oriented as (IV) than as (V). Experiments are in hand with the object of obtaining evidence of such orientation in compounds of this type.

#### EXPERIMENTAL.

*2:6-Dinitro-3-methyl-, 2:4-Dinitro-5-methyl-, and 2:6-Dinitro-4-methyl-2'-hydroxydiphenylamines.*—2:3:4-, 3:4:6-, or 3:4:5-Trinitrotoluene (4 g.), *o*-aminophenol (4 g.; 2 equivs.), and benzene (240 c.c.) were boiled for 4 hours under reflux, nitrous fumes being evolved; the mixture was then cooled and filtered. In the case of 2:3:4-trinitrotoluene the filtrate was evaporated to dryness, and the residue crystallised four times from dilute alcohol; 2:6-dinitro-2'-hydroxy-3-methyldiphenylamine was then obtained in reddish-purple needles (3 g.), m. p. 148° (Found: N, 14.7.  $C_{13}H_{11}O_5N_3$  requires N, 14.5%).

In the second case the filtrate was evaporated to small bulk and, while it was still hot, boiling light petroleum was added until precipitation commenced. On cooling, a brown solid separated which, crystallised from benzene and light petroleum, gave 2:4-dinitro-2'-hydroxy-5-methyldiphenylamine as a deep purple-brown, micro-crystalline powder (2.7 g.), m. p. 203° (Found: N, 14.8%).

Crystallised from methyl alcohol or from somewhat diluted acetic acid, this compound separated as an orange-red solid of the same m. p.

In the third case the tarry solid obtained on evaporation of the benzene was crystallised repeatedly from dilute alcohol; 2:6-dinitro-2'-hydroxy-4-methyldiphenylamine was then obtained in lustrous purple-brown needles, m. p. 152° (Found: N, 14.4%).

2-Chloro-6-nitro-2'-hydroxy-3-methyldiphenylamine.—A solution of 3:4-dinitro-*o*-chlorotoluene (2.3 g.) and *o*-aminophenol (5 g.) in alcohol (150 c.c.) was boiled under reflux for 20 hours, and cooled. Water and a little hydrochloric acid were then added and the precipitated tarry mass was extracted with boiling light petroleum; the precipitate obtained from the cooled extract was crystallised from the same solvent, 2-chloro-6-nitro-2'-hydroxy-3-methyldiphenylamine being obtained in purple-red needles (1 g.), m. p. 106° (Found: N, 10.2.  $C_{13}H_{11}O_3N_2Cl$  requires N, 10.0%).

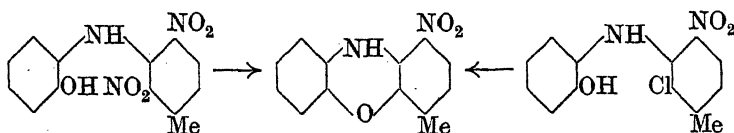
2:4-Dinitro-2'-hydroxy-3:6-dimethoxydiphenylamine.—This was prepared from trinitroquinol dimethyl ether (2.6 g.) and *o*-aminophenol (2.1 g.) in benzene (100 c.c.) as before. The reaction mixture was cooled, the liquid filtered and heated to boiling, and boiling light petroleum (200 c.c.) added. The precipitate produced on cooling was crystallised from benzene and light petroleum, 2:4-dinitro-2'-hydroxy-3:6-dimethoxydiphenylamine being obtained in brown prisms (1.5 g.), m. p. 186° (Found: N, 12.6.  $C_{14}H_{13}O_7N_3$  requires N, 12.5%).

2:4-Dinitro-2'-hydroxy-5:6'-dimethyl-, 2:6-Dinitro-2'-hydroxy-4:6'-dimethyl-, and 2:4:6-Trinitro-2'-hydroxy-6'-methyldiphenylamines.—3:4:6- and 3:4:5-Trinitrotoluenes and picryl chloride were each heated with 2 equivalents of 2-amino-*m*-cresol in benzene under reflux for 4 hours, and the solutions cooled and filtered. In the first and second cases the filtrates were evaporated to dryness, and the residues crystallised repeatedly from dilute alcohol; there were then obtained 2:4-dinitro-2'-hydroxy-5:6'-dimethyldiphenylamine as brick-red prisms, m. p. 173° (Found: N, 14.1.  $C_{14}H_{13}O_5N_3$  requires N, 13.9%), and 2:6-dinitro-2'-hydroxy-4:6'-dimethyldiphenylamine as purple plates, m. p. 198° (decomp.) (Found: N, 14.0%). In the third case light petroleum was added to the filtered solution, and the precipitate crystallised from benzene and light petroleum; 2:4:6-trinitro-2'-hydroxy-6'-methyldiphenylamine was then obtained as a bright crimson, microcrystalline powder, m. p. 176° (Found: N, 16.7.  $C_{13}H_{10}O_7N_4$  requires N, 16.8%).

Formation of Phenoxazines.—The general method adopted was to dissolve the diphenylamine compound (1 g.) in 1% aqueous sodium

hydroxide (25 c.c.) and heat the solution on the water-bath for a time varying from a few minutes to 2 hours according to the nature of the compound undergoing reaction. The phenoxazine, if formed, was precipitated and the time necessary for reaction was indicated by the amount of precipitate. Nitrite, or in one case chloride, was detected in the solution after reaction. The yields were excellent.

2 : 6-Dinitro-2'-hydroxy-3-methyldiphenylamine gave 1-nitro-4-methylphenoxazine, which separated from somewhat diluted acetic acid as a dark violet powder, m. p. 169° (Found : N, 11.9.  $C_{13}H_{10}O_3N_2$  requires N, 11.6%). The same compound was obtained from 2-chloro-6-nitro-2'-hydroxy-3-methyldiphenylamine, this result showing which of the two nitro-groups in 2 : 6-dinitro-2'-hydroxy-3-methyldiphenylamine is the reactive one :



2 : 6-Dinitro-2'-hydroxy-4-methyldiphenylamine gave 1-nitro-3-methylphenoxazine, almost black needles, m. p. 165°, from light petroleum (Found : N, 11.8%). 2 : 4-Dinitro-2'-hydroxy-3 : 6-dimethoxydiphenylamine gave 3-nitro-1 : 4-dimethoxyphenoxazine, crimson needles, m. p. 173°, from benzene and light petroleum (Found : N, 9.5.  $C_{14}H_{12}O_5N_2$  requires N, 9.7%). 2 : 4 : 6-Trinitro-2'-hydroxy-6'-methyldiphenylamine gave 1 : 3-dinitro-9-methylphenoxazine, deep purple prisms, m. p. 224°, from benzene (Found : N, 14.7.  $C_{13}H_9O_5N_3$  requires N, 14.6%). 2 : 6-Dinitro-2'-hydroxy-4 : 6'-dimethyldiphenylamine gave 1-nitro-3 : 9-dimethylphenoxazine, a violet powder, m. p. 162°, from benzene (Found : N, 11.6.  $C_{14}H_{12}O_3N_2$  requires N, 11.4%). 2 : 4-Dinitro-2'-hydroxy-5-methyl-, 2 : 4-dinitro-2'-hydroxy-6'-methyl-, and 2 : 4-dinitro-2'-hydroxy-5 : 6'-dimethyl-diphenylamines were not converted into phenoxazines under the above conditions, no precipitate formed, and no nitrite was produced.

3-Bromo-4 : 6-dinitrotoluene.—A hot alcoholic solution of 4 : 6-dinitro-*m*-tolylhydrazine (5 g.) (Brady and Bowman, J., 1921, 119, 894) was treated with successive small quantities of cupric bromide (30 g.), the mixture was cooled, and the liquid filtered. The filtrate was heated with a little concentrated hydrochloric acid and hydrogen peroxide to oxidise any cuprous bromide and poured into water. The precipitate obtained, after crystallising from alcohol, gave 3-bromo-4 : 6-dinitrotoluene in pale yellow needles, m. p. 101° (Found : N, 10.5.  $C_7H_5O_4N_2Br$  requires N, 10.7%).

*2:4-Dinitro-2'-methoxy-N-methyldiphenylamine*.—This was prepared by heating *N*-methyl-*o*-anisidine (3 g.) and 2:4-dinitrochlorobenzene (5 g.) together with a little anhydrous zinc chloride for 6 hours in an oil-bath at 130–140°. The product was distilled in steam to remove unchanged dinitrochlorobenzene, the solid residue extracted with boiling dilute hydrochloric acid, and the insoluble matter crystallised from alcohol; 2:4-dinitro-2'-methoxy-*N*-methyldiphenylamine was then obtained in yellow needles, m. p. 169° (Found: N, 14.3.  $C_{14}H_{13}O_5N_3$  requires N, 13.9%). The methoxyl group could not be demethylated by treatment with an aqueous or glacial acetic acid solution of hydrogen bromide.

*N*-Methyl-*o*-aminophenol decomposes when heated above 80°. No reaction occurred when it was boiled for many hours in benzene with 2:4-dinitrochlorobenzene or 3-bromo-4:6-dinitrotoluene.

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### CLV.—*The Preparation of Diphenyl Ethers.*

By (Miss) ROSALIND VENETIA HENLEY.

It has been shown by Groves, Turner, and Sharp (J., 1929, 512) that the use of copper-bronze in the preparation of 2-nitrodiphenyl ethers is unnecessary, since it does not increase the yield, and hampers manipulation. The following experiments have been done in order to try to determine the most favourable conditions for the preparation of such ethers, and if possible to eliminate the necessity of extensive purification, owing to the presence of much unchanged material. The effects of different proportions of halogenonitro-compound, phenol, and potassium hydroxide were studied, also the variation of time and temperature, and the use of copper, and the elimination of water, in the operations.

The method used in the condensations was as follows: the water was added to the potassium hydroxide, which was then fused. The phenol was added to the potassium hydroxide, and the two were heated until all the solid had dissolved. The halogenonitro-compound was then added, and the mixture was heated in a metal-bath, in a flask fitted with a short air-condenser. The mixture was then diluted with water, alkali was added, and the oil was extracted with carbon tetrachloride, washed with water, dried over sodium sulphate, and distilled in a vacuum, the purity of the product being determined by its constant boiling point.



*Series A.—Variation of the proportion of phenol and potassium hydroxide.*

	I.	II.	III.	IV.
<i>o</i> -Chloronitrobenzene ...	1 mol.	1 mol.	1 mol.	1 mol.
Phenol .....	1 mol.	1.5 mols.	1.75 mols.	3 mols.
Potassium hydroxide ...	1 mol.	1.25 mols.	1.33 mols.	2 mols.
Water .....	0.1 mol.	0.1 mol.	0.1 mol.	0.1 mol.
Yield, % .....	68	70	72.4	60.5

The condensation was effected at 160—180°, for 2 hours.

The most favourable conditions are those given in experiment III.

*Series B.—Variation of the time of condensation.*

*Experiment I.* The conditions used in experiment III of series A were repeated, the time of the experiment being varied. When the mixture was heated for  $\frac{1}{2}$  hour only, the reaction was incomplete, since the yield of 2-nitrodiphenyl ether was only 57%.

*Experiment II.* When the condensation was prolonged for 4 hours, the yield was 73%, showing that no improvement had been obtained.

*Series C.—Variation of the temperature of condensation.*

*Experiment I.* The conditions used in Experiment III, series A were repeated in the following experiments: When the mixture was heated at 200—210° for 1 hour, a yield of 95.5% of ether was obtained.

*Experiment II.* The same experiment was repeated, the condensation being allowed to occur for only  $\frac{1}{2}$  hour; an 84% yield was obtained, showing that the reaction was less complete.

*Experiment III.* A further experiment was done by heating the mixture at 240° for 1 hour, but the yield was only 90%, showing that no improvement had occurred.

The condensation was effected under the conditions of experiment III, series A, but with omission of the water (0.1 mol.); the yield was only 63%.

When experiment III, series A, was repeated in the presence of copper-bronze, the yield obtained was 72%, showing that no benefit is derived from its use, even when the more favourable proportions of phenol and potassium hydroxide are taken.

*Series D (a).*—In order to determine whether the conditions described in the previous experiments were generally applicable to diphenyl ethers, a series of experiments was performed with different phenols, *o*-chloronitrobenzene being the halogenonitro-compound. A control set of experiments was performed; equimolecular proportions of halogenonitro-compound, phenol, and potassium

hydroxide were used, the condensation being effected at 200—210° for 1 hour. The amount of water used was 0.1 mol.

Phenol ...	<i>o</i> -Chlorophenol	<i>p</i> -Chlorophenol	<i>o</i> -Cresol	<i>m</i> -Cresol	<i>p</i> -Cresol
Yield of ether, %	80	66	72	70	73

*Series D* (b).—The series was repeated under the conditions of experiment I, series C.

Phenol ...	<i>o</i> -Chlorophenol	<i>p</i> -Chlorophenol	<i>o</i> -Cresol	<i>m</i> -Cresol	<i>p</i> -Cresol
Yield of ether, %	91	86	85	87	87

Comparison of the two series shows that the yields are increased between 10—20% by using the increased proportions of phenol and potassium hydroxide.

The fifth experiment in series D (b) was repeated, 95 g. of *o*-chloronitrobenzene, 114 g. of *p*-cresol, and 45 g. of potassium hydroxide being used. At the end of the reaction, the condensation mixture was shaken with very dilute alkali solution until cold; a crystalline meal then separated. After being dried in the air, this weighed 129 g. (94% yield). As a result of the improved conditions worked out, it is possible to prepare ethers similar to the above, without extraction with a solvent, and subsequent vacuum distillation.

*Series E*.—The comparison of yields obtained by using different halogenonitro-compounds was also made.

*Experiment I*. 2:5-Dichloronitrobenzene was condensed with phenol, under the conditions described in the series of experiments D (a), and the yield of ether obtained was 74%. When the experiment was repeated under the conditions of experiments D (b), the yield was increased to 85%.

*Experiment II*. According to Fox and Turner (this vol., p. 1115), when 2:5-dibromonitrobenzene is condensed with phenol at 160—180° for 6 hours, 1 mol. of halogenonitro-compound, 1 mol. of phenol, 1 mol. of potassium hydroxide, and 0.1 mol. of water being used, the yield of 4-bromo-2-nitrodiphenyl ether is 48% of the theoretical. When the condensation was effected under the conditions of experiments D (b), the yield was increased to 85%.

It appears, therefore, that the best conditions for the preparation of substituted diphenyl ethers consist in having increased proportions of phenol and potassium hydroxide, and in working at a temperature not below 200°.

My thanks are due to Dr. E. E. Turner for much helpful advice during this work.

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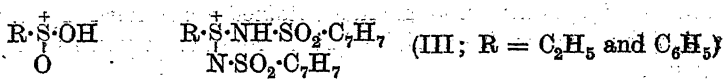
CLVI.—*The Preparation of Compounds analogous in Structure to Sulphinic Acids but containing p-Toluenesulphonimido-groups in Place of Oxygen Atoms. Phenyl- and Methyl-p-toluenesulphonimido-sulphine-p-toluenesulphonylimines:*

By SYDNEY GEORGE CLARKE, JOSEPH KENYON, and HENRY PHILLIPS.

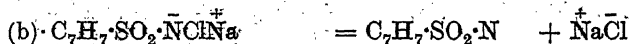
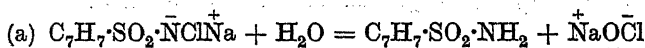
THE resolution of *dl*-*m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine (I) (Clarke, Kenyon, and Phillips, J., 1927, 188), corresponding to the *dl*-sulphoxide (II) resolved by Harrison, Kenyon, and Phillips (J., 1926, 2079), provided experimental evidence that the *p*-toluenesulphonimido-group could become linked



with sulphur in the same manner as the oxygen atom of a sulphoxide. It has now been found that compounds can be prepared analogous in structure to sulphinic acids but containing two *p*-toluenesulphonimido-groups in place of the two oxygen atoms of the sulphinic acid group. Two examples of this new class of compound have been



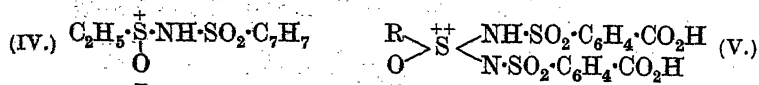
prepared in which R = C<sub>2</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>5</sub> respectively. They can be obtained readily by the action of chloramine-T on solutions of sodium phenyl and ethyl mercaptides. The formation of these compounds, under the experimental conditions employed, provides evidence that in aqueous solution chloramine-T not only undergoes hydrolysis as in equation (a) but also dissociates to give a neutral *p*-toluenesulphonimido-radical as indicated in equation (b).



From a consideration of these equations it would be anticipated that, by the use of a suitable anhydrous solvent in which sodium chloride is insoluble, the production of the *p*-toluenesulphonimido-radical would be favoured and the hydrolysis of chloramine-T suppressed. This deduction receives support from the fact that

a greater yield of the phenyl compound is obtained from solutions of phenyl mercaptan in acetic acid or in pyridine than from solutions of the mercaptan (as sodium salt) in water. Even when a large excess of chloramine-T is employed in these reactions, the same two compounds are obtained, indicating that the sulphur atoms of the mercaptans show little or no tendency to combine with three *p*-toluenesulphonimido-groups to produce compounds analogous to sulphonic acids. The chemical properties of *phenyl-* and *ethyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimines* are also in agreement with the view that the large *p*-toluenesulphonimido-groups exert a protective influence on the central sulphur atoms and cause them to be far less reactive than the corresponding sulphur atoms of sulphinic acids. For example, sulphinic acids react readily with bromine to yield sulphonyl bromides and condense with formaldehyde, benzoquinone (Hinsberg, *Ber.*, 1884, **27**, 3359) and azobenzene (Hantzsch and Glogauer, *Ber.*, 1897, **30**, 2565), but, under the same experimental conditions, ethyl- and phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimines do not react with these reagents. A similar difference in behaviour exists between sulphilimines and sulfoxides; *m*-carboxyphenylmethylsulphine-*p*-toluenesulphonylimine (I) cannot be converted into a derivative of sexavalent sulphur, whereas the corresponding sulfoxide (II) readily forms a sulphone. When heated with concentrated hydrochloric acid, the new sulphonylimines slowly decompose, producing the corresponding disulphides, sulphonic acids, and *p*-toluenesulphonamide. The quantities of *p*-toluenesulphonamide obtained are in harmony with the view that two *p*-toluenesulphonimido-groups are present in each molecule.

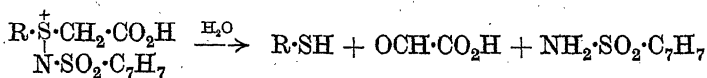
It was not found possible to replace the imido hydrogen atoms in these compounds by methyl groups by the agency of either methyl sulphate or methyl iodide under various experimental conditions. During such attempted methylations, the compounds decomposed, *p*-toluenesulphon-monomethyl- and -dimethyl-amides being the chief products. From the decomposition products of the methylation of ethyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine, *ethyl-p-toluenesulphonylsulphinamide* (IV) was isolated.



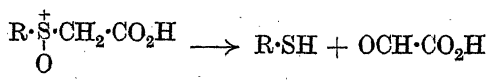
The sulphonylimines undergo oxidation much less readily than do the corresponding sulphinic acids. They are unaffected by perhydrol, but, in alkaline solution, they are converted by potassium permanganate into tribasic acids (V). These new acids yield

*p*-sulphonamidobenzoic acid on hydrolysis with concentrated acids, but the experimental evidence that they contain oxygen atoms linked to the central sulphur atoms is not conclusive.

Ethyl- and phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimines were also isolated from the products of the interaction of ethyl- and phenyl-thiolacetates with chloramine-T. The failure to obtain the sulphilimines of these salts by this means can be attributed either to the instability of these sulphilimines in the presence of water, or, alternatively, to the preferential formation



of the corresponding sulfoxides, which decompose in a similar manner (Pummerer, *Ber.*, 1909, **42**, 2282; 1910, **43**, 1404) :



The ethyl- and phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimines isolated from these reactions doubtless arise from the interaction of the chloramine-T with the mercaptans produced during the decomposition of either the sulphilimine or the sulfoxide or both these compounds, as indicated in the above equations.

#### EXPERIMENTAL.

*Ethyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine* (III; R = Et).—(a) *From ethyl mercaptan.* Chloramine-T (58 g., 2 mols.) in warm water (150 c.c.) was added to a solution of ethyl mercaptan (6.2 g.) in sodium hydroxide (3*N*, 33 c.c.), and after an hour the solution was acidified with dilute sulphuric acid. The *ethyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine* (20 g.) produced was extracted from the precipitate obtained by means of dilute sodium carbonate solution, in which the *p*-toluenesulphonamide (12.8 g.) simultaneously precipitated was insoluble. By acidification of the sodium carbonate extract, the new compound was precipitated. After crystallisation from ethyl alcohol, it had m. p. 189° (decomp.), either alone or when mixed with the *ethyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine* prepared from ethylthiolacetic acid as described below.

(b) *From ethylthiolacetic acid.* A warm solution of chloramine-T (240 g.) in water (1000 c.c.) was added to an alkaline solution of ethylthiolacetic acid (48 g.) in sodium hydroxide (3*N*, 200 c.c.). After 3 days, the solid which had separated was removed by filtration, and, on acidification of the alkaline filtrate, *ethyl-p-toluene-*

sulphonimidodisulphine-*p*-toluenesulphonylimine was precipitated. It was purified as described above and then weighed 20.4 g. and had m. p. 189° (decomp.) [Found: C, 47.8; H, 5.0; N, 7.0; S, 23.7.  $C_{16}H_{20}O_4N_2S_3$  requires C, 48.0; H, 5.0; N, 7.0; S, 24.0%. 0.4000 G. required 0.0400 g. of sodium hydroxide for neutralisation to phenolphthalein: equiv., 400.  $(C_{16}H_{19}O_4N_2S_3)H$  requires equiv., 400. Found for the *silver* salt, after drying at 120–130°: Ag, 21.6.  $C_{16}H_{19}O_4N_2S_3Ag$  requires Ag, 21.3%].

The solid which was removed by filtration was triturated with chloroform (150 c.c.); *p*-toluenesulphonamide (83 g., m. p. 138°) remained undissolved. From the chloroform extract a neutral substance (3.1 g.) was isolated which, after crystallisation from ethyl alcohol, had m. p. 128° (decomp.). This neutral compound decomposed at its m. p., yielding an inflammable vapour, and left a residue (97% of the original) which, after crystallisation from ether and light petroleum, had m. p. 108–112°. On hydrolysis with hot concentrated hydrochloric acid, the neutral compound gave 15% of its weight of *p*-toluenesulphonamide (Found: C, 34.4; H, 3.7; N, 4.1; S, 18.2; Cl, 20.9%, corresponding fairly closely with the empirical composition  $C_{10}H_{12}O_4NCl_2S_2$ ).

*The Chemical Properties and Reactions of Ethyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine.*—*Hydrolysis.* Dilute sulphuric acid was without action on the compound, but the clear solution obtained by heating it (1.0 g.) with 50% sulphuric acid deposited *p*-toluenesulphonamide (0.82 g.) on cooling [Theoretical quantity for  $C_2H_5S(C_7H_7O_2SN)_2$ , 0.86 g.]. A similar result was obtained by the use of concentrated hydrochloric acid.

*Oxidation.* Formation of 
$$Et \begin{array}{c} \diagup \\ O \end{array} S^{++} \begin{array}{c} \diagdown \\ \diagup \end{array} \begin{array}{l} NH \cdot SO_2 \cdot C_6H_4 \cdot CO_2H \\ N \cdot SO_2 \cdot C_6H_4 \cdot CO_2H \end{array}$$
 To ethyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine (8 g.) dissolved in dilute aqueous sodium hydroxide, small quantities of a saturated solution of potassium permanganate (in all, 13.6 g.) were added during 3 hours. After the passage of sulphur dioxide to dissolve the manganese dioxide, the resulting solution was acidified with dilute sulphuric acid; the new compound (8.2 g., m. p. 260–262°) was then precipitated. After three recrystallisations from alcohol, it had m. p. 275–276° (decomp.), which was unchanged by reprecipitation of the compound from its solution in sodium hydroxide solution and further recrystallisation from alcohol [Found: S, 20.6%. 0.5000 G. neutralised 0.1204 g. of sodium hydroxide: equiv., 166.  $(C_{16}H_{13}O_9N_2S_3)H_3$  requires S, 20.2%; equiv., 159.  $(C_{16}H_{13}O_8N_2S_3)H_3$  requires S, 20.8%; equiv., 154]. This acid (1.0 g.) was heated under reflux with concentrated hydrochloric acid (25 c.c.) for 1.5 hours. . . . *p*-Sulphon-

amidobenzoic acid (0.68 g.), m. p. 284—285°, either alone or when mixed with an authentic specimen of that compound, was filtered from the cold reaction mixture (Found: S, 16.1. Calc. for  $C_7H_7O_4NS$ : S, 15.9%).

*Action of methylating agents. Formation of ethyl-p-toluenesulphonylsulphinamide*,  $Et\cdot SO\cdot NH\cdot SO_2\cdot C_6H_7$ . The sulphonylimine (8 g.), dissolved in *N*-sodium hydroxide (40 c.c.), was treated with methyl sulphate and sufficient sodium hydroxide to maintain the solution alkaline, until the oily precipitate which separated from the hot reaction mixture ceased to increase in amount. On cooling, this oily precipitate solidified; after crystallisation from alcohol, it was obtained (1.8 g.) with m. p. 78—79°, either alone or when mixed with *p*-toluenesulphondimethylamide prepared by the action of methyl sulphate on an alkaline solution of *p*-toluenesulphonamide (Found: S, 16.1.  $C_9H_{13}O_2NS$  requires S, 16.1%). The filtrate from this *p*-toluenesulphondimethylamide was concentrated, and, after several days, it deposited a crystalline sodium salt. On acidification of an aqueous solution of this salt, *ethyl-p-toluenesulphonylsulphinamide* (3.5 g.) was precipitated, and this, after crystallisation from alcohol, had m. p. 120° (Found: S, 25.6; N, 5.6.  $C_9H_{13}O_3NS_2$  requires S, 25.9; N, 5.6%).

By treatment of *ethyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine* in boiling toluene containing anhydrous potassium carbonate with methyl sulphate, only a mixture of *p*-toluenesulphonmonomethyl- and -dimethyl-amides was obtained. Similarly, the silver salt of the sulphonylimine, when heated under reflux with methyl iodide, gave *p*-toluenesulphondimethylamide. Each of these methylation reactions yielded small quantities of other products which were not identified.

*Phenyl-p-toluenesulphonimidodisulphine-p-toluenesulphonylimine* (III; R = Ph).—(a) *From thiophenol*. (i) *In water*. To thiophenol (5.5 g., 1 mol.), dissolved in dilute aqueous sodium hydroxide, a warm aqueous solution of chloramine-T (28.3 g., 2 mols.) in water (100 c.c.) was added. The granular precipitate which was thrown down consisted mainly of *p*-toluenesulphonamide, but gave some diphenyl disulphide (5 g.), m. p. 61—62°, when extracted with benzene. The warm filtrate, on cooling, deposited the crystalline sodium salt of phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine, m. p. 226° (Found: Na, 4.8.  $C_{20}H_{19}O_4N_2S_3Na$  requires Na, 4.9%). A warm aqueous solution of this salt gave, on acidification, phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine which, after crystallisation from alcohol, had m. p. 152—153° [Found: C, 52.9; H, 4.6; N, 6.5; S, 21.3.  $C_{20}H_{20}O_4N_2S_3$  requires C, 53.1; H, 4.5; N, 6.3; S, 21.4%. 0.2000 G. neutralised

0.0176 g. of sodium hydroxide: equiv., 455. ( $C_{20}H_{19}O_4N_2S_3$ )H requires equiv., 448]. The *silver* salt was a white curdy precipitate obtained by vigorously stirring a solution of the sodium salt to which silver nitrate had been added [Found (after drying at  $110^\circ$ ): Ag, 19.9.  $C_{20}H_{19}O_4N_2S_3$ Ag requires Ag, 19.5%].

(ii) *In acetic acid*. Chloramine-T (280 g.) was shaken with a hot solution of thiophenol (55 g.) in glacial acetic acid (300 c.c.). After being heated on a steam-bath for 15 minutes, the mixture was poured into water. The solid material which separated was extracted with benzene to remove diphenyl disulphide, and then digested with hot dilute sulphuric acid. A heavy viscous oil remained which crystallised on cooling and, after recrystallisation, gave phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine (40 g.), m. p.  $152-153^\circ$ . A further quantity of this compound (20 g.) was obtained by acidification of the filtrate from the solid material which separated when the reaction mixture was poured into water.

(iii) *In pyridine*. The reaction was carried out as described in (ii). When the reaction mixture was poured into water, only diphenyl disulphide separated. The sulphonylimine was precipitated by the addition of acid to the aqueous pyridine. Thiophenol (5 g.) gave 5 g. of the sulphonylimine.

(b) *From phenylthiolacetic acid*. Chloramine-T (85 g.) was shaken with a solution of the sodium salt of phenylthiolacetic acid (23.5 g.) in hot water. After being heated for 30 minutes on the steam-bath, the mixture was cooled and the water together with some crystalline material was decanted from the compact solid mass which had formed on the bottom of the flask. Diphenyl disulphide (12 g.), m. p.  $60-61^\circ$ , was extracted from this mass with benzene. The residual solid was recrystallised from alcohol and proved to be the sodium salt of phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine (4 g.), m. p.  $227-228^\circ$ , either alone or when mixed with the sodium salt prepared directly from sodium thiophenoxide. The crystalline material, mentioned above, was dissolved in hot water and reprecipitated as an oil by the addition of acid. This oil solidified on cooling and proved to be the sulphonylimine, m. p.  $153^\circ$ , either alone or when mixed with the sulphonylimine prepared from sodium thiophenoxide.

*The Chemical Properties and Reactions of Phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine.—Hydrolysis.* When heated on a steam-bath for 30 minutes with concentrated hydrochloric acid (100 c.c.), the sulphonylimine (3 g.) gradually lost its crystalline character and gave place to an oil. The hot acid, decanted from the oil, deposited *p*-toluenesulphonamide (1.4 g.) on cooling: on con-



centration, the filtrate from this sulphonamide deposited a further quantity (0.3 g.) of this substance. The filtrate from this second crop of sulphonamide was taken to dryness in a vacuum; the residue (benzenesulphonic acid) gave benzenesulphonamide, after successive treatment with phosphorus pentachloride and ammonium carbonate.

The oil, obtained as described above, solidified on cooling. After being freed from *p*-toluenesulphonamide by extraction with sodium hydroxide solution and recrystallised from light petroleum, it gave diphenyl disulphide (0.7 g.), m. p. and mixed m. p. 60–61°.

*Oxidation.* The preparation of  $\text{Ph-O-S}^{\text{++}}\begin{matrix} \text{NH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} \\ \text{N}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} \end{matrix}$ .

Perhydrol was without action on hot aqueous solutions of either phenyl-*p*-toluenesulphonimidodisulphine-*p*-toluenesulphonylimine or its sodium salt. The latter compound was, however, successfully oxidised with potassium permanganate. To a solution of the sodium salt (4.4 g.) in water (50 c.c.), heated on a steam-bath, a saturated aqueous solution of potassium permanganate was added during 3 hours. In all, 6.6 g. of permanganate (about 3 mols. oxygen) were added: a further small addition was not decolorised. After passage of sulphur dioxide to dissolve the manganese mud, hydrochloric acid was added; a colourless crystalline solid then separated. After three recrystallisations from alcohol, it (1.2 g.) was obtained with m. p. 201° (decomp.) (Found: N, 5.4; S, 17.9.  $\text{C}_{20}\text{H}_{16}\text{O}_9\text{N}_2\text{S}_3$  requires N, 5.3; S, 18.3%.  $\text{C}_{20}\text{H}_{16}\text{O}_8\text{N}_2\text{S}_3$  requires N, 5.5; S, 19.0%).

When a suspension of this compound (1.0 g.) in concentrated hydrochloric acid was heated under reflux for 1 hour, a silky crystalline compound was produced, m. p. 284–285°, either alone or when mixed with *p*-sulphonamidobenzoic acid.

*Action of methylating agents.* To a solution of the sulphonylimine (9 g.) in dilute aqueous sodium hydroxide heated to 90–95°, methyl sulphate (21 g., 9 mols.) was added gradually with vigorous shaking. During the addition an oil separated which solidified on cooling; after recrystallisation from alcohol, it had m. p. 79–80°, either alone or when mixed with *p*-toluenesulphonodimethylamide. The aqueous filtrate from this sulphonamide gave, on evaporation, a small quantity of a basic oil which was not identified.

The finely divided sulphonylimine (4.5 g.) and potassium carbonate (4.0 g.) were heated under reflux in toluene containing methyl sulphate (2 g.) for 7 hours. The toluene was removed and the portion of the residue insoluble in water was proved to consist of a mixture of *p*-toluenesulphon-monomethyl- and -dimethyl-amides, together with some diphenyl disulphide and unchanged sulphonyl-

imine. The only product which could be isolated from the products of the interaction of the silver salt of the sulphonylimine with methyl iodide was diphenyl disulphide.

The authors wish to thank the Government Grant Committee of the Royal Society and also Imperial Chemical Industries, Ltd., for grants which have defrayed much of the cost of this investigation.

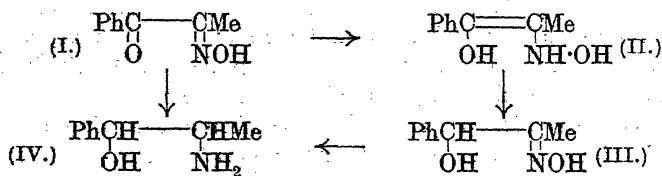
BATTERSEA POLYTECHNIC, S.W.11.

[Received, April 3rd, 1930.]

## CLVII.—*Nor-dl*-ephedrine and *Nor-dl-ψ*-ephedrine.

By DONALD HOLROYDE HEY.

As previous attempts (this vol., p. 18) to obtain *nor-dl*-ephedrine and *nor-dl-ψ*-ephedrine (IV) from *isonitrosopropiophenone* (I) by direct reduction had proved unsatisfactory, attention was directed to the *oxime* of phenylacetylcarbinol (III): this on reduction with sodium amalgam in dilute acetic acid solution readily gave a viscous oil, which on treatment with hydrochloric acid gave *nor-dl*-ephedrine hydrochloride together with a small quantity of *nor-dl-ψ*-ephedrine hydrochloride. By introducing suitable modifications of the methods of obtaining phenylacetylcarbinol described in the literature the yield of this compound has been more than doubled, which therefore greatly improves the efficiency of this method of synthesis. A similar method, depending on the reduction of the oximes of ketonic alcohols of the type  $\text{OH}\cdot\text{CHPh}\cdot\text{COR}$ , has been recorded by Tiffeneau and Lévy (*Compt. rend.*, 1926, 183, 969).



In the reduction of *isonitrosopropiophenone* (I), as carried out by Rabe (*Ber.*, 1912, 45, 2166), in addition to a small quantity of the amino-alcohol (IV), a second compound was obtained, melting at 112°, which was described as the oxime of phenylacetylcarbinol (III). Hartung and Munch (*J. Amer. Chem. Soc.*, 1929, 51, 2262) also observed the formation of a second compound, but only when *isonitrosopropiophenone* was reduced catalytically in the absence of hydrochloric acid. This compound melted at 108–110° and was not identified. The results of the present investigation give further support to Rabe's contention that the compound isolated by him was the oxime of phenylacetylcarbinol, which agrees in all its

properties with those of the oxime here described. The compound isolated by Hartung and Munch has also now been identified as the oxime of phenylacetylcarbinol. A specimen, kindly submitted by Dr. Hartung, produced no depression of melting point when mixed with the oxime described in this communication, and further observations by Dr. Hartung confirm this view. While there are many examples of the reduction of  $\alpha$ -oximino-ketones to amino-ketones, their reduction to oximino-alcohols is apparently very rare. However, the formation of this oxime in the reduction of isonitroso-propiophenone, though unusual, would not necessarily signify that the oximino-group is less susceptible to the action of the reducing agent than the carbonyl group (compare Hartung and Munch, *loc. cit.*), since it is not improbable that, under the conditions employed, the oxime is formed by molecular rearrangement of an intermediate hydroxylamino-alcohol (II).

#### EXPERIMENTAL.

*dl*-Mandelamide was prepared in excellent yield by the method of McKenzie and Wren (J., 1908, 93, 310).

*Preparation of Phenylacetylcarbinol.*—By observing the following modifications in the methods of Wren (J., 1909, 95, 1592) and of Tiffeneau and Lévy (*Bull. Soc. chim.*, 1925, 37, 1247) the yields of phenylacetylcarbinol were increased to about 50% of the theoretical yield. Well-powdered *dl*-mandelamide (20 g.) was added very slowly to an excess of the Grignard reagent (7 mols.), well cooled in ice. The latter was prepared from 22 g. of magnesium, 140 g. of methyl iodide, and 250 c.c. of dry ether. When all the amide had been added, the mixture was kept at room temperature for 1 hour and then gently boiled under reflux for 12 hours. The solution, well cooled in ice, was decomposed by the gradual addition of ice and dilute sulphuric acid. No unchanged amide separated and the liberated phenylacetylcarbinol was extracted with ether and dried. It distilled as a pale yellow oil (9.5 g.) at 135–137°/24 mm. (Found: C, 71.8; H, 6.6. Calc. for  $C_9H_{10}O_2$ : C, 72.0; H, 6.7%). The semicarbazone, from boiling toluene, melted at 194°.

The 2:4-dinitrophenylhydrazone was prepared by warming an alcoholic solution of 2:4-dinitrophenylhydrazine and phenylacetylcarbinol. Orange needles separated on cooling, which after recrystallisation from alcohol melted at 170° (Found: N, 17.1.  $C_{15}H_{14}O_5N_4$  requires N, 17.0%).

The oxime of phenylacetylcarbinol was prepared by boiling under reflux for 2 hours a solution of 5 g. of the ketone, 2.6 g. of hydroxylamine hydrochloride, and 1.5 g. of sodium hydroxide in water with the addition of sufficient alcohol to make the solution homogeneous

at the temperature of boiling. When cold, the solution was acidified and the oxime was extracted repeatedly with ether and dried. Evaporation of the ether left an oily residue, which when kept in a vacuum deposited a crystalline solid (4 g.). Recrystallisation from hot water gave the oxime in white needles, m. p.  $112.5^{\circ}$  (Found: C, 65.55; H, 6.3; N, 8.4.  $C_9H_{11}O_2N$  requires C, 65.45; H, 6.7; N, 8.5%). A small quantity of a less soluble compound was also formed, which crystallised from alcohol in small white needles, m. p.  $231^{\circ}$ . This was in all probability phenylmethylglyoxime (Borsche, *Ber.*, 1907, 40, 740) (Found: N, 15.8. Calc. for  $C_9H_{10}O_2N_2$ : N, 15.7%).

*Reduction of Phenylacetylcarbinol Oxime.*—60 G. of 3% sodium amalgam were gradually added to a solution of the oxime (2 g.) in dilute acetic acid. After 6 hours, the mixture was made alkaline and extracted several times with ether. After drying over solid caustic potash, evaporation of the ether left a colourless viscous oil, which was dissolved in warm hydrochloric acid. The solid which separated on standing was recrystallised from absolute alcohol, nor-*dl*-ephedrine hydrochloride being obtained, m. p.  $192^{\circ}$  after a second recrystallisation (Found: Cl, 18.7. Calc. for  $C_9H_{13}ON, HCl$ : Cl, 18.9%). From the mother-liquor a small quantity of nor-*dl*- $\psi$ -ephedrine hydrochloride was obtained, which after several recrystallisations from absolute alcohol melted at  $169^{\circ}$  (Found: Cl, 18.9%) (compare Nagai and Kanao, *Annalen*, 1929, 470, 157).

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### CLVIII.—*The Constitution of Sinactine (1-Tetrahydro-epiberberine).*

By KAKUJI GOTO and ZENJIRO KITASATO.

SINACTINE, the natural occurrence of which was prophesied by W. H. Perkin and his co-workers (Perkin, J., 1918, 113, 494; Haworth, Koepfli, and Perkin, J., 1927, 2261), is present in *Sinomenium acutum*, Reht and Wills, in minute quantities and has been isolated from the root as a sub-alkaloid of sinomenine by Goto and Sudzuki (*Bull. Chem. Soc. Japan*, 1929, 4, 220). These authors assigned to it the formula  $C_{19}H_{21}O_4N$  and suggested that it might contain the tetrahydropapaverine skeleton. We have now found that its formula is  $C_{20}H_{21}O_4N$  and that it contains the tetrahydroberberine skeleton.

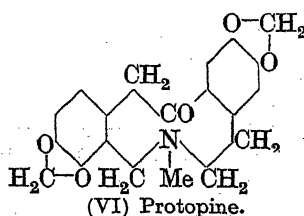
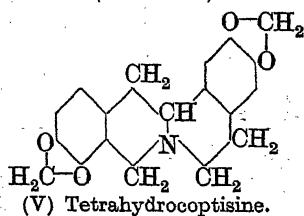
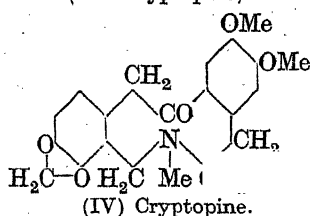
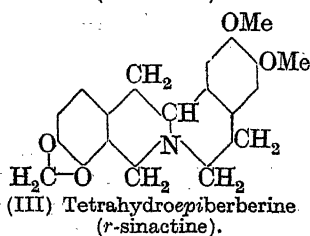
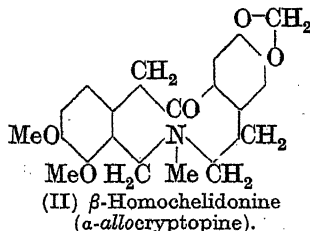
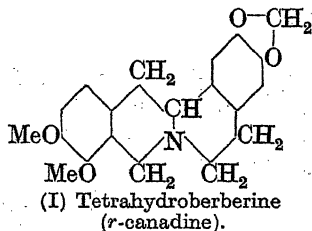
Sinactine contains two methoxy-groups and one methylenedioxy-group. Its absorption spectra resemble closely those of tetra-

hydroberberine and tetrahydropapaverine (*loc. cit.*), an *M*/1000-alcoholic solution producing an absorption band at a frequency of about 3500: this similarity suggests a very close structural relation between these compounds (compare Dobbie and Lauder, J., 1903, 83, 614; Kitasato, *Acta Phytochim.*, 1927, 3, 229).

By the action of mild oxidising agents, such as iodine in alcoholic solution, on sinactine a base is produced which forms an intensely orange chloride,  $C_{20}H_{18}O_4NCl$ , corresponding to the berberinium salt. From this base, by reduction, *r*-sinactine is obtained. This melts at  $168^\circ$  and has properties very similar to those of tetrahydroepiberberine (III), m. p.  $169-170^\circ$  (Perkin, J., 1918, 113, 512; Haworth and Perkin, J., 1926, 1777): direct comparison of *r*-sinactine with a specimen of synthetic tetrahydroepiberberine, kindly sent to us by Dr. R. D. Haworth, and the melting point of a mixture of the two substances definitely established their identity.

From the foregoing, it appears that sinactine is *l*-tetrahydroepiberberine (III), that is, the positions of the methylenedioxy-group and the two methoxy-groups in sinactine are the reverse of their positions in tetrahydroberberine (I).

The relationship of the ten-membered ring alkaloids is still more clearly brought out when their formulæ are compared:



## EXPERIMENTAL.

The roots of *Sinomenium acutum* are digested three times with 0.5% hydrochloric acid at the ordinary temperature and the combined extracts are made alkaline with sodium carbonate and shaken thrice with chloroform. The chloroform solution is treated with dilute hydrochloric acid to remove alkaloids (sinomenine, etc.) other than sinactine. Sinactine hydrochloride accumulates in chloroform when this is repeatedly used in the extraction of the alkaloids without evaporation; it is so sparingly soluble in water (0.74%) that it can easily be purified from sinomenine.

Sinactine, m. p.  $175^{\circ}$ , is obtained in needles from a solution of its hydrochloride by means of ammonia or in colourless slender prisms by crystallisation from alcohol. It is sparingly soluble in cold methyl or ethyl alcohol, almost insoluble in water, and readily soluble in chloroform. The solution of a crystal in a drop of acetic acid gives at first no coloration on the addition of sulphuric acid, but gradually a violet tint develops [Found by microanalysis: C, 71.0, 70.5, 71.05; H, 6.4, 6.3, 6.3; N, 4.4; OMe, 18.9.  $C_{18}H_{15}O_2N(OMe)_2$  requires C, 70.8; H, 6.2; N, 4.2; OMe, 18.3%]. The alkaloid has  $[\alpha]_D - 312^{\circ}$  in chloroform ( $c = 1$ ;  $l = 1$ ). It contains a methylenedioxy-group, as it gives a copious precipitate on treatment with phloroglucinol-sulphuric acid; it has no phenolic hydroxyl group, since it does not react with ferric chloride, potassium ferricyanide, or a diazo-solution; and it has no methylimino-group, since after being heated for 2 hours at about  $300^{\circ}$  with hydriodic acid and ammonium iodide it gives no precipitate with silver nitrate.

The hydrochloride separates from water in colourless needles, m. p. about  $272^{\circ}$  (decomp.). The chloroplatinate forms crystals which begin to darken at  $240^{\circ}$  and melt at  $245-247^{\circ}$ .

*r-Sinactine*.—Sinactine (0.5 g.) is dissolved in boiling alcohol, and a 2% alcoholic solution of iodine added in portions. The colour of the iodine disappears rapidly and an orange crystalline precipitate separates (compare Perkin, J., 1918, 113, 514). After  $\frac{1}{2}$  hour's boiling, the precipitate is collected, treated with sulphurous acid to remove a trace of iodine, and recrystallised from boiling water; orange-yellow needles are obtained which darken at  $275^{\circ}$  and decompose at about  $300^{\circ}$ . This iodide is suspended in water and digested with freshly precipitated silver chloride for an hour. After removal of silver compounds, the filtrate and washings are concentrated considerably and treated with hydrochloric acid. The dehydrosinactine chloride that separates after a few hours is recrystallised from hot water by addition of hydrochloric acid:

the orange needles obtained have all the properties of *epiberberin*-ium chloride described by Perkin (*loc. cit.*, p. 516).

Dehydrosinactine chloride (1 g.) is reduced for 5 hours with glacial acetic acid (10 c.c.), 15% sulphuric acid (100 c.c.), and zinc dust. When sodium chloride is added to the filtered solution, a pale yellow precipitate separates: this is collected, washed with dilute sodium chloride solution, dissolved in boiling alcohol, and decomposed by very dilute aqueous ammonia. The base obtained is optically inactive and crystallises from much alcohol in colourless needles, m. p. 168° (Found: C, 71.0; H, 6.2. Calc.: C, 70.8; H, 6.2%). Mixed with synthetic tetrahydro*epiberberine* (m. p. 166–167°), it melts at 166°. Moreover, a solution of the base in glacial acetic acid, on addition of concentrated sulphuric acid, gives a colourless solution which gradually turns deep violet: tetrahydro*epiberberine* shows the same reaction. The hydrochloride of *r*-sinactine separates from much water in fine needles, which decompose at about 286°. The methosulphate, prepared in the same way as tetrahydro*epiberberine* methosulphate (Perkin, *loc. cit.*), crystallises from methyl alcohol in large colourless prisms, m. p. 257° (decomp.). The iodide melts at 275°.

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## CLIX.—*Studies of Electrolytic Polarisation. Part IX.*

### *Complex Cyanides: (c) Zinc, Cadmium, and Mercury.*

By SAMUEL GLASSTONE.

FROM previous studies (J., 1929, 690, 702) it was concluded, in contrast to the views of Le Blanc and Schick (*Z. Elektrochem.*, 1903, 9, 636; *Z. physikal. Chem.*, 1903, 46, 213) and of Foerster (*Z. Elektrochem.*, 1907, 13, 561), that the cathode potential-*C.D.* curves and the current efficiency for metal deposition in the electrolysis of complex cyanides depend on (a) the variation of electrode potential with increasing ratio of cyanide to metal in the solution, and (b) the relation of the potential in the presence of excess of cyanide to that at which hydrogen evolution occurs. If the solution under examination is one in which an increase of the cyanide concentration causes an appreciable alteration of potential, *i.e.*, if it corresponds with a position on the metal ion-cyanide titration curve where there is a marked inflexion, polarisation should be appreciable. On the other hand, very little polarisation should result when the addition of cyanide has only a small influence on the electrode potential; this occurs when the solution already

contains an excess of cyanide. If the cathode potential remains below that requisite for the evolution of hydrogen, the efficiency for metal deposition is 100%; but if the *C.D.* exceeds a value at which the rate of deposition of metal is greater than the rate of diffusion of the appropriate ions to the electrode, the cathode potential rises rapidly, the efficiency for metal deposition falls off, and hydrogen evolution commences. If the hydrogen potential is attained before the limiting *C.D.* is reached, the current efficiency decreases at this point, but there is no rapid increase of cathode potential. Since all the polarisation observed in the electrolysis of complex cyanides is due ultimately to concentration changes, and not to the slowness of any chemical reaction, it can be decreased by vigorous stirring of the electrolyte.

The above views, based on observations on complex silver and copper cyanides, have now been tested and confirmed by similar experiments involving electrometric titrations of salts of zinc, cadmium, and mercury with sodium cyanide solutions, together with cathode-potential and current-efficiency measurements at various *C.D.*'s.

Zinc dissolves spontaneously in alkali cyanide solutions with the evolution of hydrogen, since the electrode potential  $\text{Zn}|\text{KCN}$  is about  $-1.25$  volts; hence the electrolytic behaviour of complex zinc cyanide solutions was expected to be similar to that of the cuprocyanides (J., 1929, 702). Cadmium and mercury are not attacked by potassium cyanide solution in the absence of air; on electrolysis their complex cyanides were, therefore, expected to give results similar to those obtained with argentocyanide solutions (J., 1929, 690). The limited observations made by Spitzer (*Z. Elektrochem.*, 1905, **11**, 345) and by Höing (*ibid.*, 1916, **22**, 286) on zinc, and by Efremov (*Ann. Inst. Polyt. Ural*, 1927, **6**, 111) on cadmium, were seen to support these conclusions.

#### EXPERIMENTAL.

The experimental methods were similar to those already used for the study of silver and copper complex cyanides. With zinc and cadmium the electrometric titrations were performed on the corresponding sulphates in *N/5*-solutions; the electrolysis solutions were made from the same salts by the addition of appropriate amounts of cyanide. Sodium cyanide was used almost exclusively throughout this work; independent experiments showed that potassium cyanide gave exactly similar results. For the observations with the mercury cathode, a pure specimen of mercuric cyanide was used; as this substance is almost a non-electrolyte, a small amount of sodium sulphate was added to the solution.



It is noteworthy that mercuric cyanide is stable in contact with metallic mercury, whereas under these conditions most other mercuric salts are unstable and tend to form mercurous salts. Mercurous cyanide, however, is unstable and decomposes immediately into mercuric cyanide and mercury (Abel, *Z. anorg. Chem.*, 1901, 26, 379). The explanation of this behaviour lies in the fact that mercuric cyanide yields only a very small concentration of mercuric ions in solution; from observations made in the course of the present work the mercuric-ion concentration (assumed equal to the activity) is about  $10^{-21}$  g.-ion per litre in  $N/5$ -solutions of the cyanide. According to Abel (*loc. cit.*, p. 375),  $[\text{Hg}_2^{++}]/[\text{Hg}^{++}]$  is equal to 120 when mercuric and mercurous ions are in equilibrium with metallic mercury; hence the concentration of mercurous ions in the mercury-mercuric cyanide system is about  $10^{-19}$  g.-ion per litre. Mercurous salts are generally more highly ionised than corresponding mercuric salts (compare Lowry, *Trans. Faraday Soc.*, 1928, 24, 1), and so only an extremely small concentration of mercurous cyanide can co-exist with mercuric cyanide and mercury. The latter salt is, therefore, stable and the former unstable.

Cathode-potential measurements were made by the methods described in previous papers of this series. Attempts were made to determine the current efficiencies for metal deposition, but only with cadmium was a systematic study possible. Zinc dissolves so readily in solutions containing the slightest excess of free cyanide that even at high *C.D.*'s there was a net loss in weight of the cathode. A rough indication of the efficiencies can, however, be obtained from the cathode-potential measurements. A satisfactory investigation of the current efficiency with a mercury cathode was prevented by experimental difficulties, but approximate determinations were made with an amalgamated copper electrode as well as with one of liquid mercury; the results indicated that the metal was discharged almost entirely as bivalent ions.

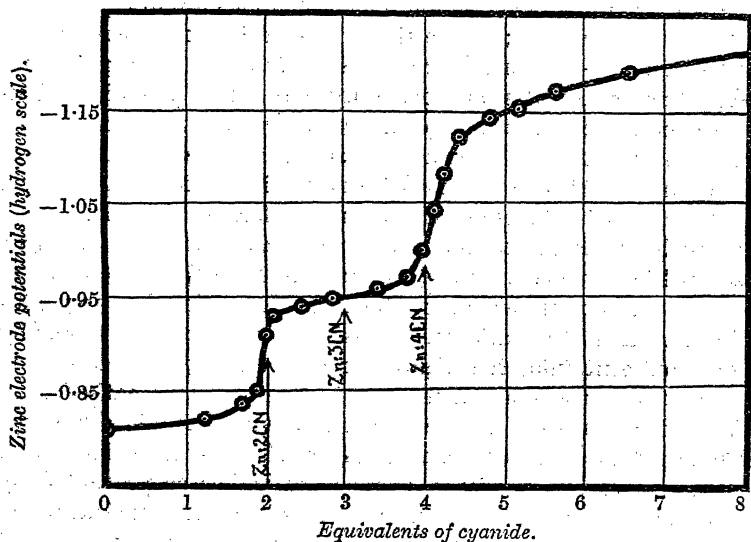
Unless otherwise stated, experiments were carried out at room temperature ( $15^\circ$ ). All electrode-potential measurements are expressed on the normal hydrogen scale.

### Results.

*Zinc.*—The electrometric titration curve of zinc sulphate solution with sodium cyanide, a zinc electrode being used as indicator, is shown in Fig. 1. The precipitate of zinc cyanide dissolves completely when the ratio  $\text{Zn} : \text{CN} = 1 : 4$ , in approximately  $N/10$ -solutions (see Treadwell, *Chem.-Ztg.*, 1914, 38, 1230; Corbet, J., 1926, 3190); this fact, together with the shape of the titration curve, suggests that  $\text{Zn}(\text{CN})_4^{--}$  is the chief complex ion present in solution. The

$p_H$  of the  $\text{Na}_2\text{Zn}(\text{CN})_4$  solution is about 10, and the reversible potential of a hydrogen electrode in it is  $-0.57$ ; the reversible zinc potential is  $-0.99$  volt. In the electrolysis of such a solution, therefore, hydrogen may be expected to be liberated at the cathode instead of metal, but the high overvoltage of hydrogen at a zinc cathode prevents this happening. Actually, it has been observed that hydrogen bubbles appear at a zinc electrode in a complex cyanide solution at a potential of  $-1.18$  volts; even at less negative potentials, however, some of the current will be utilised in the discharge of hydrogen ions, since the resulting atoms are removed by diffusion

FIG. 1.



or by depolarisation with air. It is clear, therefore, that 100% efficiency for zinc deposition is not to be expected from solutions containing cyanides.

The titration curve shows that cathodic polarisation cannot be as marked as with silver and copper, since the sudden rise of potential occurring when the ratio  $\text{CN}:\text{Zn}$  exceeds 4:1 is only from  $-0.99$  to  $-1.14$ ; beyond this, the zinc electrode potential rises gradually to  $-1.24$  volts, which is the value in a  $0.5N$ -sodium cyanide solution. Since the free evolution of hydrogen commences at  $-1.18$  volts, the subsequent change of potential of the zinc cathode should be similar to that in a simple cyanide solution in which hydrogen discharge is the only cathodic process (Table I, last column).

The actual cathode potentials (C.P.) and current efficiencies (C.E.) recorded in Table I are in agreement with the predictions

made from a study of the titration curve. Solution I was  $M/10$  with respect to  $\text{Na}_2\text{Zn}(\text{CN})_4$ , and Solution II contained in addition  $N/5$ -sodium cyanide. The current efficiencies, which are in any case very rough, could not be determined for Solution II for the reason given on p. 1239. Experiments were also made with Solution I stirred (500 r.p.m.) at  $15^\circ$ , and unstirred at  $70^\circ$ .

TABLE I.  
*Cathode potentials and current efficiencies.*  
Solution I.

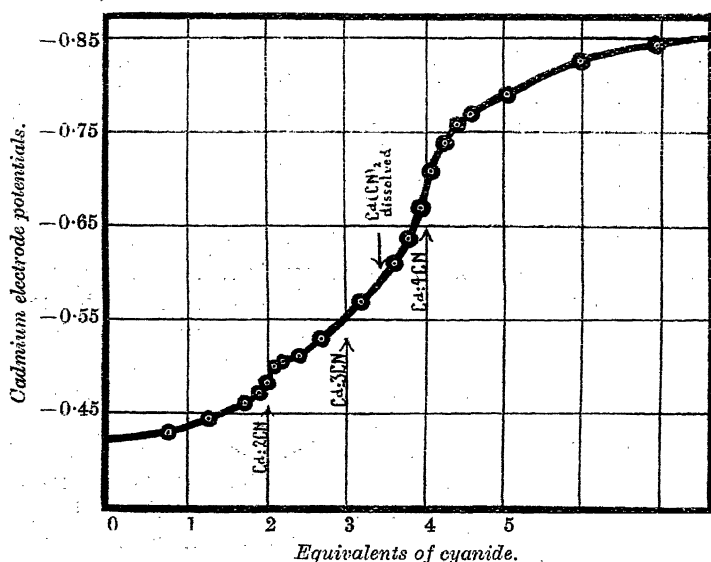
C.D. $\times 10^4$ (amps./ $\text{cm}^2$ ).	Unstirred at $15^\circ$ .		Stirred at $15^\circ$ .		Unstirred at $70^\circ$ .		Solution II.	$N/5$ - NaCN.
	C.P.	C.E.	C.P.	C.E.	C.P.	C.E.	C.P.	C.P.
—	-0.99	—	-0.99	—	-0.99	—	-1.22	-1.24
1.0	-1.04	—	—	—	-1.01	—	-1.24	-1.26
2.0	-1.06	—	-1.00	—	-1.02	—	-1.26	-1.27
4.0	-1.09	—	-1.01	—	-1.06	—	-1.29	-1.31
8.0	-1.16	52	-1.03	—	-1.08	—	-1.33	-1.34
12	-1.27	33	-1.07	48	-1.14	51	-1.40	-1.41
20	-1.34	30	-1.14	40	-1.20	41	-1.44	-1.45
40	-1.39	26	-1.24	36	-1.28	36	-1.47	-1.50

It is to be noted that stirring the electrolyte and raising the temperature have not the same marked influence on the current efficiency for zinc deposition as for copper (*loc. cit.*); this is because the polarisation in the former case is smaller, and so stirring and raising the temperature, which tend to decrease polarisation, cannot be relatively so effective. Further, since the cathode potential for zinc deposition from cyanide solutions is always more negative than that required for the reversible discharge of hydrogen ions, the removal of accumulated hydrogen as a result of stirring will increase the proportion of current devoted to the discharge of these ions, and the efficiency of zinc deposition must decrease in consequence. Similarly, at high temperatures the overvoltage for hydrogen evolution is decreased, and a larger proportion of the current will be utilised in liberating hydrogen than for the same cathode potential at lower temperatures. All the observed results may, therefore, be explained without the necessity of assuming that the complex zincicyanide ion dissociates *slowly* into its constituents.

During the course of this work, it was noted that zinc sulphate solution dissolves appreciable amounts of zinc cyanide: 1 l. of  $M$ -solution dissolves about 0.003 g.-mol. at  $15^\circ$ , and 0.01 g.-mol. at  $70^\circ$ . This suggests, as in the case of silver (see Hellwig, *Z. anorg. Chem.*, 1901, 25, 157), that a complex zinc cyanide *kation*, possibly  $[\text{Zn}_2(\text{CN})_2]^{++}$ , is formed; these complex ions, rather than simple zinc ions, may be actually discharged at the cathode during the electrolysis of cyanide solutions (compare J., 1929, 700, 712).

*Cadmium.*—The electrode potential–titration curve for  $M/5$ -cadmium sulphate solution with sodium cyanide and a cadmium electrode, is shown in Fig. 2; the slight inflexion corresponding with the formation of  $\text{Cd}(\text{CN})_2$  indicates that this substance is comparatively soluble. The electrode potential of cadmium in the system containing cadmium and cyanide in the ratio 1 : 2 is  $-0.49$  volt; hence the solubility of cadmium cyanide in water is of the order of  $10^{-3}$  g.-mol. per litre. This is of a similar order to the solubility of zinc cyanide, but is appreciably greater than that of silver and copper cyanides. It is of interest that at least 1 c.c. of  $N$ -sodium cyanide solution

FIG. 2.



must be added to 10 c.c. of  $N$ -cadmium sulphate solution before a permanent precipitate of cadmium cyanide is formed; the latter is thus appreciably soluble in the sulphate solution, possibly as a result of the formation of a complex kation of the type  $[\text{Cd}_2(\text{CN})_2]^{++}$ . The shape of the titration curve when the ratio  $\text{CN} : \text{Cd}$  exceeds 2 : 1, and the fact that the precipitate of cadmium cyanide dissolves completely when the ratio is *ca.* 3.5 : 1 (see also Corbet, *loc. cit.*), suggests that at least two complex ions,  $\text{Cd}(\text{CN})_3^-$ , or perhaps  $[\text{Cd}(\text{CN})_3(\text{H}_2\text{O})]^-$ , and  $\text{Cd}(\text{CN})_4^{2-}$  are present in solution (see also Pines, *J. Czech. Chem. Comm.*, 1929, 1, 387).

During electrolysis, the cathodic polarisation of cadmium in a solution containing  $\text{Cd} : \text{CN} = 1 : 4$  should be of the same order as with zinc; a rapid rise of potential can occur only between  $-0.67$

and  $-0.82$  volt, and this will be followed by a more gradual rise to about  $-0.95$  volt, the potential of cadmium in  $N/2$ -sodium cyanide solution. There is, however, an important difference between cadmium and zinc as regards hydrogen evolution; it has been found that the gas commences to be evolved freely from a cadmium cathode in sodium cyanide solution at a potential of about  $-1.1$  volts, a value distinctly more negative than that of cadmium in the same solution. It is clear, therefore, that during the electrolysis of complex cadmicyanide solutions the metal should be deposited at almost 100% efficiency, unless the *C.D.* is such that the rate of deposition exceeds the rate of diffusion of cadmium compounds to the cathode. At this limiting *C.D.* the potential will rise and the current efficiency for metal deposition fall. It may be calculated by the method described in a previous paper (J., 1929, 697) that for an  $M/10$ -solution of a cadmium salt the limiting *C.D.* at which the rates of deposition and diffusion are equal is about  $0.0055$  amp./cm.<sup>2</sup>. This value, as in the case of argentocyanide solutions, should be independent of the amount of free cyanide present,\* but should depend on (a) the concentration of the cadmium salt, (b) the temperature of the solution, and (c) whether the solution is stirred or not. Raising the temperature or stirring the electrolyte should raise the limiting *C.D.* for 100% deposition, but dilution should bring about a decrease.

The results obtained in the investigations on the electrolysis of cadmium cyanide solutions are given in Table II. Solution I contained Cd and CN in the ratio of 1 to 4, and in Solution II the ratio was 1 to 6; the concentration of cadmium salt was  $M/10$  in each original electrolyte.

These results are in agreement with the views already expressed; the limiting *C.D.* for 100% efficiency of metal deposition is about  $0.006$  amp./cm.<sup>2</sup> in the  $M/10$ - and  $0.00055$  in the  $M/100$ -solutions. As in the work on silver, the effect of stirring at 500 r.p.m., or of raising the temperature to  $70^\circ$ , is to increase the limiting *C.D.* in the dilute solution four- or five-fold. It is of interest that the limiting *C.D.* for 100% efficiency of metal deposition in an  $M/10$ -cadmium sulphate solution is  $0.006$  amp./cm.<sup>2</sup>; this result indicates, in agreement with expectation, that the simple  $\text{Cd}^{++}$  and the complex  $\text{Cd}(\text{CN})_4^{--}$  ions diffuse at almost the same rate. The limiting *C.D.* is thus independent of the actual concentration of  $\text{Cd}^{++}$  ions, but depends primarily on the total cadmium concentration.

\* If the solution contains a large excess of free cyanide the efficiency may be somewhat lowered, since hydrogen ions may be discharged to replace the gas removed by diffusion and depolarisation.

TABLE II.

Solution I.										
C.D. $\times 10^4$ (amps./cm. <sup>2</sup> ).	Unstirred.		Stirred.		Diluted 10-fold.		Diluted and stirred.		Diluted, at 70°.	
	C.P.	C.E.	C.P.	C.E.	C.P.	C.E.	C.P.	C.E.	C.P.	C.E.
—	-0.67	—	-0.67	—	-0.65	—	-0.65	—	-0.65	—
1.0	-0.72	—	—	—	-0.69	—	—	—	—	—
2.0	-0.75	—	—	—	-0.76	—	-0.69	—	-0.70	—
3.0	-0.77	—	—	—	-0.84	—	—	—	—	—
4.0	-0.78	—	-0.73	—	-0.89	100	-0.71	—	-0.74	—
5.0	—	—	—	—	-0.93	—	—	—	—	—
6.0	—	—	—	—	-1.19	54	-0.74	—	-0.78	—
10	-0.82	—	-0.76	—	-1.37	22	-0.79	—	-0.81	—
20	-0.86	—	-0.78	—	-1.46	18	-0.83	100	-0.85	100
30	-0.89	—	—	—	—	—	-1.15	82	-1.20	80
50	-0.91	100	-0.80	—	—	—	-1.36	57	-1.28	65
60	-1.00	—	—	—	—	—	-1.44	30	-1.35	38
70	-1.30	90	—	—	—	—	—	—	—	—
100	-1.40	83	-0.84	100	—	—	—	—	—	—
170	—	—	-0.89	—	—	—	—	—	—	—
200	—	—	-1.26	92	—	—	—	—	—	—

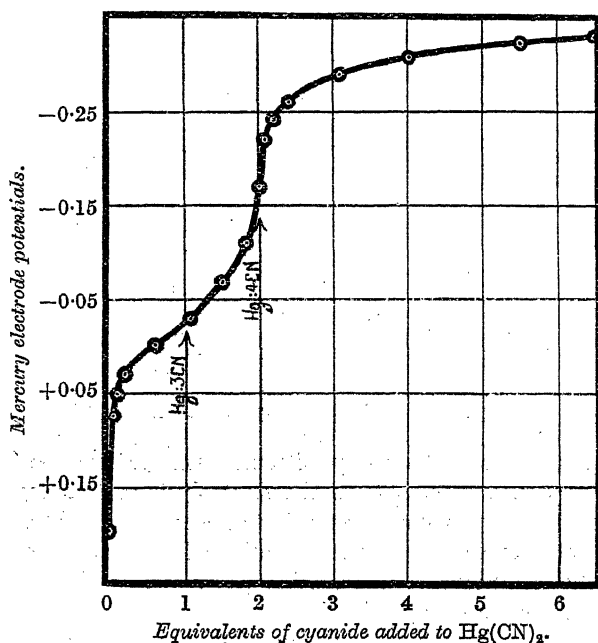
Solution II.										
C.D. $\times 10^4$ (amps./cm. <sup>2</sup> ).	Unstirred.		Diluted 10-fold.		Diluted and stirred.		Diluted, at 70°.			
	C.P.	C.E.	C.P.	C.E.	C.P.	C.E.	C.P.	C.E.		
—	-0.84	—	-0.80	—	-0.80	—	-0.80	—		
1.0	—	—	-0.85	—	-0.81	—	—	—		
2.0	—	—	-0.89	—	—	—	—	—		
3.0	—	—	-0.92	—	—	—	—	—		
4.0	-0.90	—	-0.96	—	-0.85	—	—	—		
5.0	—	—	-0.99	100	—	—	—	—		
6.0	—	—	-1.27	73	-0.90	—	—	—		
10	-0.92	—	-1.35	48	-0.93	—	-0.91	—		
20	-0.94	—	-1.45	30	-0.98	100	-0.99	100		
30	-0.95	—	—	—	-1.30	74	-1.28	70		
50	-0.98	100	—	—	-1.45	35	—	—		
70	-1.32	91	—	—	—	—	—	—		
100	-1.41	84	—	—	—	—	—	—		

**Mercury.**—Since mercuric salts, other than the cyanide, are unstable in the presence of mercury, an  $M/10$ -solution of the latter salt was used for the electrometric titration with sodium cyanide and a mercury indicator electrode; the variation of mercury electrode potential with varying  $Hg:CN$  ratios is shown in Fig. 3. The shape of the curve indicates that  $Hg(CN)_4^{--}$  is the main ion formed when alkali cyanide is added to mercuric cyanide, but the absence of any marked horizontal portion between the  $Hg:CN$  ratios 1:2 and 1:4 (i.e., between 0 and 2 added equivs.) suggests that the ion  $Hg(CN)_3^-$  is also formed to some extent. Since mercuric cyanide is soluble in water, it is not possible to verify this conclusion by observations on the solubility in the presence of alkali cyanide. From the titration curve, it may be seen also that on electrolysis the cathode potential of mercury in a solution of mercuric cyanide should alter with increasing polarising  $C.D.$  at first rapidly from 0.18 to 0.03, more slowly to -0.15, rapidly again to -0.25, and finally more gradually to about -0.35 volt. In a solution of  $Na_2Hg(CN)_4$ , the polarisation should be marked at low  $C.D.$ 's, since the mercury potential rises from -0.15 to -0.25 for quite small changes in the  $Hg:CN$  ratio. If the electrolyte contains excess of

free cyanide there should be very little polarisation even at appreciable *C.D.*'s.

As the rate of diffusion of the mercuricyanide ion is probably similar to that of other ions (diffusion coefficient, 1.2 approx.), the limiting *C.D.* for 100% efficiency of mercury deposition should be about 0.006 amp./cm.<sup>2</sup>; above this *C.D.* some of the current must be utilised in the discharge of hydrogen ions. Since the overvoltage for hydrogen evolution at a mercury electrode is more than 0.7, the cathode potential for the liberation of this gas from cyanide

FIG. 3.



solutions will be about -1.3 volts. Hence, in the electrolysis of mercuricyanide solutions, the potential beyond the limiting *C.D.* must rise rapidly from -0.35 to -1.3 volts, and at the same time the current efficiency should fall. The actual results obtained were in agreement with these anticipations. Cathode-potential measurements made by means of the commutator were trustworthy only up to the limiting *C.D.*, for above this point the rate of fall of potential on switching off the current—as might be anticipated from the factors already mentioned—was too great to allow of accurate extrapolation being made. The potentials in Table III are therefore only for *C.D.*'s at which there is no tendency for hydrogen

evolution to occur; the highest *C.D.* quoted for any particular electrolyte may be regarded as the limiting value for 100% efficiency of mercury deposition in that solution. On account of the difficulties of working with a mercury cathode, only a limited number of current-efficiency measurements were made; these, as well as others with an amalgamated copper electrode, indicated that at all *C.D.*'s given in Table III the metal-deposition efficiency was about 100%. Solution I was *M*/10-mercuric cyanide containing some sodium sulphate to increase the conductance; Solution II was *M*/10- $\text{Na}_2\text{Hg}(\text{CN})_4$ , and Solution III contained in addition 0.4*N*-sodium cyanide solution.

TABLE III.  
*Cathode potentials.*

<i>C.D.</i> $\times 10^4$ (amps./cm. <sup>2</sup> ).	Solution I.			Solution II.		
	I.	Diluted 5-fold.	Diluted, at 70°.	II.	Diluted 10-fold.	Solution III.
—	0.18	0.18	0.19	—0.15	—0.13	—0.33
2.0	0.08	0.02	0.09	—0.21	—0.19	—0.36
4.0	—	—0.03	0.04	—0.24	—0.24	—0.37
5.0	—	—0.05	—	—	—0.27	—
6.0	0.01	—0.07	—	—0.27	—0.29	—0.39
8.0	—	—0.15	—	—0.28	—	—
12	—0.02	—0.31	—0.03	—	—	—
20	—0.04	—	—0.06	—0.30	—	—0.41
30	—0.06	—	—0.16	—0.33	—	—0.42
50	—0.19	—	—0.21	—0.34	—	—
60	—0.32	—	—0.32	—0.35	—	—0.43

These results are in harmony with the anticipations based on the general principles applicable to the electrolysis of complex cyanide solutions. As in previous cases, dilution decreases the limiting *C.D.* to an extent proportional to the reduction of concentration, whereas raising the temperature (and stirring) increases this *C.D.* The extent of cathodic polarisation is a function of the variation of the mercury potential with changes in the Hg:CN ratio; although the mercuricyanide ion probably dissociates rapidly into its constituents, there must be some polarisation in Solution II, but less in Solution III.

#### *Summary.*

(1) Cathode-potential and current-efficiency measurements have been made in solutions containing complex cyanides of zinc, cadmium, and mercury.

(2) The main factors influencing the results are (a) the variation of electrode potential with increasing ratio of cyanide to metal, (b) the potential for hydrogen evolution at the given metal, and (c) the concentration of the electrolyte.



(3) There is no reason to believe that any of the complex cyanides studied hitherto dissociate slowly.

(4) Electrometric-titration curves indicate the presence of  $\text{Zn}(\text{CN})_4^{--}$  ions in zinc solutions,  $\text{Cd}(\text{CN})_3^-$  and  $\text{Cd}(\text{CN})_4^{--}$  ions in cadmium solutions, and  $\text{Hg}(\text{CN})_3^-$  and  $\text{Hg}(\text{CN})_4^{--}$  ions in mercuric solutions.

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### CLX.—*The Acetates of Ruthenium.*

By (the late) ALFRED WILLIAM MOND.

THE ruthenium salts of the acids of the acetic series appear to be unknown. In this paper the preparation of several of the *acetates* is described. They are all of the complex basic type, as is to be expected from the position of the metal in the periodic table (compare chromium and especially iron). Though the great solubility of most of these compounds makes their purification very difficult, the analytical results indicate that definite chemical individuals were obtained.

They were made by the action of the acid on the hydroxide formed by treating ruthenium trichloride,  $\text{RuCl}_3$ , with alkali. This is generally regarded as the hydrated trioxide  $\text{Ru}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ; but Howe (*J. Amer. Chem. Soc.*, 1927, **49**, 2381) maintains that it contains quadrivalent ruthenium, and that its formula should be written  $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ , whilst Crowell and Yost (*ibid.*, 1928, **50**, 374) and Remy and Lührs (*Ber.*, 1928, **61**, 917; 1929, **62**, 200) consider that in the hydroxide, and in the more or less hydrolysed solutions of the chloride in water, the metal is partly trivalent and partly quadrivalent. This leads to a difficulty in formulating some of the acetates. Most of them are derived from a complex salt which should be written  $\text{Ru}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_4$  if the metal is quadrivalent, and  $\text{Ru}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_2(\text{OH}_2)_2$  if it is trivalent. The difference in composition for the metal and the carbon lies within the errors of analysis; but the values for the hydrogen, though rather uncertain owing to the difficulty of ensuring complete removal of the water without decomposition, agree best with the assumption that the metal is trivalent. Two of the acetates must contain trivalent ruthenium.

The first product (A) of the action of glacial acetic acid on the trioxide is  $\text{Ru}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_2(\text{OH}_2)_2$ . This on hydrolysis yields (B)  $\text{Ru}_2(\text{C}_2\text{H}_3\text{O}_2)_3(\text{OH})_3(\text{OH}_2)_2$  and (C)  $\text{Ru}_2(\text{C}_2\text{H}_3\text{O}_2)(\text{OH})_5(\text{OH}_2)_2$ . (It seems simpler to distinguish the compounds by letters, rather

than by lengthy systematic names.) These three obviously belong to one type. Two others of a different type were obtained: (D)  $\text{Ru}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_2$ , formed along with (B) in the hydrolysis of (A), and (E)  $\text{Ru}_2(\text{C}_2\text{H}_3\text{O}_2)_5(\text{OH})$ . These differed in properties from the first three, being excessively hygroscopic, and less easily reduced to the metal on ignition.

#### EXPERIMENTAL.

Pure ruthenium sponge, kindly lent by the Mond Nickel Company, was converted through the tetroxide into the trichloride, and thence by precipitation in aqueous solution with alkali into the hydroxide, which was washed, dried, and used in the subsequent work.

*Methods of Analysis.*—For the estimation of ruthenium, a weighed quantity of the compound was heated in a porcelain crucible, and then ignited strongly in a stream of hydrogen (introduced by a silica tube passing through the lid) until the weight was constant. For the two compounds (D) and (E) it was necessary, in order to prevent reaction with the crucible in the earlier stages, to wrap the sample in filter paper and heat it at first gently and then more strongly until the paper was burnt away; the subsequent reduction in hydrogen was then carried out as before.

The carbon and hydrogen were determined by combustion.

(A).  $\text{Ru}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_2(\text{OH}_2)_2$ .—Freshly prepared hydroxide was boiled for 2 hours with glacial acetic acid. The dark green, almost black, solution was filtered and concentrated on a water-bath. On cooling, a solid separated, which was filtered off and, after removal of as much as possible of the mother-liquor by pressing between filter papers, was dried in a desiccator over sulphuric acid. It formed a black crystalline powder, readily and completely soluble in water or alcohol to a deep green solution (Found: Ru, 40.0; C, 18.71; H, 3.18.  $\text{C}_8\text{H}_{18}\text{O}_{12}\text{Ru}_2$  requires Ru, 39.93; C, 18.85; H, 3.53%). A further but less pure yield was obtained from the mother-liquor.

(B).  $\text{Ru}_2(\text{C}_2\text{H}_3\text{O}_2)_3(\text{OH})_3(\text{OH}_2)_2$ .—A strong solution of the previous compound in water was boiled for about 20 minutes. It became acid, turned brown, and deposited a black precipitate. This was filtered off and dried at  $80^\circ$ . It was insoluble in water (Found: Ru, 43.9; C, 15.45; H, 3.32.  $\text{C}_6\text{H}_{16}\text{O}_{11}\text{Ru}_2$  requires Ru, 43.51; C, 15.40; H, 3.42%).

(D).  $\text{Ru}_2(\text{C}_2\text{H}_3\text{O}_2)_4(\text{OH})_2$ .—The brownish filtrate from (B) was evaporated on a water-bath. It gave no signs of crystallising, but left a black powder, very hygroscopic and readily soluble in alcohol, from which it was precipitated unchanged by ether. A drop of the concentrated aqueous solution, when evaporated on a warmed microscope slide, formed a network of brownish-black crystals

(Found: Ru, 43.08; C, 19.62; H, 3.34.  $C_8H_{14}O_{10}Ru_2$  requires Ru, 42.96; C, 20.28; H, 2.96%).

(C).  $Ru_2(C_2H_3O_2)(OH)_5(OH_2)_2$ .—On prolonged treatment with water, the tetra-acetate (A) undergoes further hydrolysis; after 24 hours' treatment with dilute acetic acid at  $100^\circ$ , the solution on evaporation left a residue of a black powder, completely soluble in water or alcohol to a brownish-green solution, and approximating in composition to  $Ru_2(C_2H_3O_2)_2(OH)_4(OH_2)_2$ . When this was boiled with water, nearly all the ruthenium was precipitated as a black powder of the composition of (C) (Found: Ru, 53.30; C, 6.10; H, 3.01.  $C_2H_{12}O_9Ru_2$  requires Ru, 53.05; C, 6.26; H, 3.13%).

(E).  $Ru_2(C_2H_3O_2)_5OH$ .—Freshly prepared ruthenium hydroxide was dissolved in 50% acetic acid, and the deep green solution filtered and evaporated to dryness. A black, very hygroscopic residue remained, which gave a deep green solution in water or alcohol, and was precipitated from the latter as a black powder (Found: Ru, 39.5; C, 23.41; H, 3.5.  $C_{10}H_{16}O_{11}Ru_2$  requires Ru, 39.47; C, 23.28; H, 3.10%).

*Ruthenium Formates*.—Ruthenium hydroxide dissolves readily in 50% formic acid, and the deep green solution on evaporation leaves a black crystalline residue very soluble in water, but, unlike the acetates, insoluble in alcohol. The composition of this approximates to the formula  $Ru_3(HCO_2)_7(OH)_2 \cdot 5H_2O$  (Found: Ru, 41.0; C, 11.2; H, 1.96.  $C_7H_{19}O_{21}Ru_3$  requires Ru, 41.00; C, 11.29; H, 2.55%). Belloni (*Arch. Pharm.*, 1909, 247, 123) obtained in the same way from ferric hydroxide a formate of the similar formula  $Fe_3(HCO_2)_7(OH)_2 \cdot 7H_2O$ .

On prolonged heating with water, the *ruthenium formate* is partially hydrolysed, with the production of a series of yellow, brown, and black products, some soluble in water and some in alcohol, which were not further examined.

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## CLXI.—*Physicochemical Studies of Complex Acids.* *Part I. Tungstic Acid.*

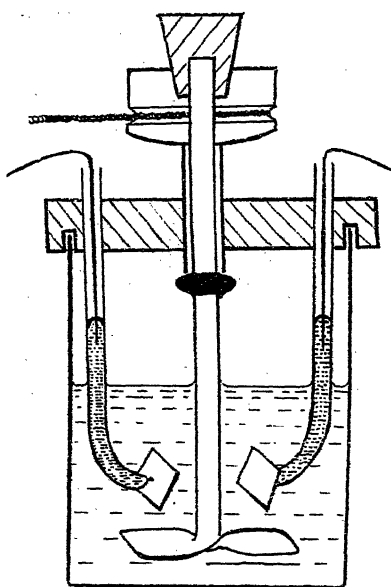
By HUBERT THOMAS STANLEY BRITTON and WILLIAM LESLIE  
GERMAN.

IN a previous communication (Britton, J., 1927, 147) it was shown that in solution tungstic acid reacts with sodium hydroxide as a dibasic acid, but that in all other respects its behaviour is abnormal. The present paper deals with potentiometric and conductometric

experiments which have been carried out to gain some insight into its nature. For this purpose, it was possible to use the quinhydrone electrode successfully in acid solutions.

When a concentrated solution of sodium tungstate is treated with an excess of hydrochloric acid, tungstic acid is usually precipitated. If, however, dilute solutions are employed, no separation occurs, the solution remaining perfectly clear. This is a surprising fact in view of the insolubility of tungstic acid in dilute acid solutions, though the freshly precipitated oxide may often be peptised by concentrated acid solutions. It might be inferred, from the approxi-

FIG. 1.



mate  $p_H$  curve given in the earlier paper, that the comparatively high concentration of hydrogen ions set up in the solution immediately after the amount of added hydrochloric acid exceeded 1.5 mols. per mol. of sodium tungstate, was caused by the liberation of tungstic acid in an ionised form, the tungstic acid hitherto produced having combined with the undecomposed sodium tungstate in the form of polytungstates. Contrary to expectation, the following work indicates that the enhanced hydrogen-ion concentration is due to free hydrochloric acid, which, on the basis of the equation  $\text{Na}_2\text{WO}_4 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{WO}_3 \cdot \text{H}_2\text{O}$ , would not

be expected to exist until 2 mols. are added, unless an inert sodium polytungstate (which could resist the attack of hydrochloric acid) were produced in the course of the reaction.

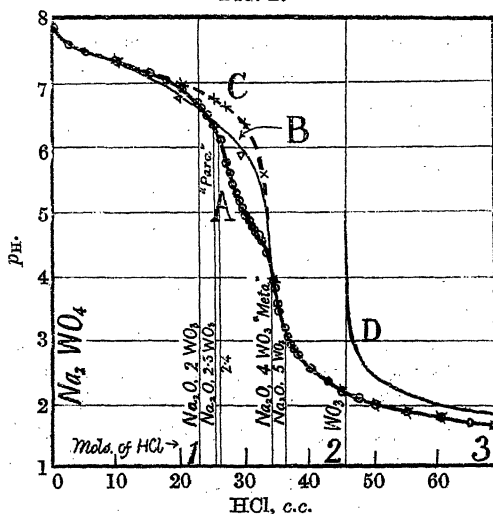
#### EXPERIMENTAL.

Quinhydrone yielded reproducible *E.M.F.*'s in all solutions of tungstates, the contact electrode being bright platinum foil attached to a platinum wire fused into the end of a glass tube containing mercury. The solutions undergoing examination were placed in beakers, to which about 0.05 g. of quinhydrone had been added. They were connected, through a salt bridge containing a saturated solution of potassium chloride, the ends of which were

plugged loosely with filter paper, to a normal calomel electrode. Before any potentials were measured, the solution was vigorously shaken mechanically. These measurements were made at room temperature, and the  $p_H$  values were calculated by using the appropriate normal reduction potential of quinone-quinol obtained from Biilmann and Krarup's formula (J., 1924, 125, 1954).

The conductometric titrations were performed in a thermostat, carefully regulated to  $25.0^\circ \pm 0.05^\circ$ , a specially designed cell being used in which efficient mechanical stirring was possible without moving the cell or disturbing the electrodes (see Fig. 1) The cell has a capacity of 150 c.c.; it is provided with a tightly fitting

FIG. 2.



ebonite cap, through which pass two glass tubes supporting the square platinum electrodes and, in the centre, a short copper tube in which the rod of the glass paddle rotates. The latter, which operates below the electrodes, is prevented from coming into contact with them by means of the rubber band placed just below the copper tube. The paddle rod is supported in the aluminium pulley wheel by means of a tightly fitting rubber bung in which it is fitted. The electrodes were platinised in the usual manner. The water used in the solutions had a specific conductivity of  $4 \times 10^{-6}$  mho.

*Reaction between Sodium Tungstate and Hydrochloric Acid.*—

(a) *Potentiometric method.* This reaction has been investigated electrometrically in solutions of various concentrations, but as the type of curve obtained in all cases is the same, reference will be made only to those relating to the more dilute solutions. In Fig. 2

are given the quinhydrone curves illustrating the course taken by the hydrogen-ion concentration when 50 c.c. of 0.05*M*-sodium tungstate were titrated with 0.1095*M*-hydrochloric acid. Curve A represents the change occurring during a titration in which about 3 minutes elapsed between each addition of acid. Curve B was constructed from  $p_H$  measurements made on solutions corresponding with various stages of the titration after they had been allowed to stand for one week. Curve C refers to data obtained from solutions corresponding with different stages of the titration after 5 minutes' boiling followed by immediate cooling to room temperature. The  $p_H$  values at different stages of the titration under these conditions are recorded in Table I. Two inflexions appear in Curve A, one of which was obscured in the curve given in the earlier paper on account of difficulties introduced by the electrodes then used. The first occurs between  $p_H$  6.3 and 3.8, the corresponding polytungstate formed varying from about 2.3 to 4.0 mols. of  $WO_3$  per mol. of  $Na_2O$ . These limits happen to be those associated with the so-called paratungstate and the metatungstate respectively. This inflexion disappears (as shown Curves B and C) when the solutions concerned are boiled or allowed to stand. The second inflexion indicates that after the metatungstate has been formed the solution rapidly acquires an acid reaction of a magnitude similar to that which would be caused by free hydrochloric acid. Curve D represents the course which would have been taken by the hydrogen-ion concentration if the hydrochloric acid had reacted with the sodium tungstate in accordance with the equation  $Na_2WO_4 + 2HCl \longrightarrow 2NaCl + WO_3 \cdot H_2O$ , on the assumptions (1) that, after the stoichiometrical

TABLE I.

0.1095 <i>N</i> . HCl, c.c.	$Na_2O : WO_3$ , mols.	$p_H$ .		
		Curve A.	Curve B.	Curve C.
0	1	7.90	8.00	8.00
11.4	0.75	7.30	7.30	7.28
22.8	0.50	6.65	6.84	6.62
34.2	0.25	3.86	5.0	5.0
39.9	0.125	2.49	2.48	2.58
45.6	0.0	2.14	2.12	2.12
50.0	Excess HCl	2.00	2.00*	1.93*
60.0	"	1.77	1.81*	1.74*
75.0	"	1.61	1.61*	1.60*

\* Some precipitation had taken place.

amount of acid has been added, the hydrogen ions are due only to the excess of hydrochloric acid, and (2) that the tungstic acid liberated has no effect. Such an assumption seemed justifiable in view of the observations of Kargin (*Kolloid-Z.*, 1929, 49, 281), who found that tungstic acid sols had  $p_H$  values of 3.69–3.68.

Curve D was obtained with the quinhydrone electrode, and relates to the addition of 0.1095*N*-hydrochloric acid to a volume (*viz.*, 95.6 c.c.) of solution equal to that of the solution in the original titration when exactly 2 mols. (45.6 c.c.) of hydrochloric acid had been added, and which contained the exact weight of sodium chloride that would have been formed if the reaction shown above had at that point been just completed. Typical data are given in Table II. Ageing and boiling had no great effect on the  $p_H$  values of the very acid solutions, in spite of the fact that the solutions to which more than 50 c.c. of hydrochloric acid had been added underwent partial precipitation of tungstic oxide.

TABLE II.

HCl, c.c.	Corresponding vol. of HCl for Curve A, c.c.	$p_H$ .		Difference, 100 [H <sup>+</sup> ].
		NaCl + HCl.	Curve A.	
4.4	50	2.44	2.00	0.64
14.4	60	2.00	1.77	0.70
24.4	70	1.77	1.67	0.44
34.4	80	1.67	1.58	0.49

Increasing the concentrations of the reactants had little effect on the reaction as indicated by  $p_H$  data. One significant difference, however, occurred in the appearance of solutions containing more than 1.5 mols. of hydrochloric acid on boiling or ageing. Thus, when 0.55*N*-hydrochloric acid and 0.250*M*-sodium tungstate were used, the solution became opalescent with 1.5 mols. and increased with more acid until coagulation ensued at  $p_H$  1.9 on ageing and at  $p_H$  1.3 after boiling. The tungstic acid formed in these experiments, therefore, first exists in a perfectly clear solution, but on being boiled or kept, it undergoes very gradual precipitation. The surprising facts are that this precipitation has very little influence on the hydrogen-ion concentration, and further, that this concentration is greater than that which can be attributed to the excess of hydrochloric acid. It was suggested in the previous paper that the tungstic acid might possibly exist in the clear acid solution in a sub-colloidal form peptised by the hydrochloric acid. Were this the case, it would appear that a little hydrochloric acid would be either adsorbed by or chemically combined with the tungstic acid, and consequently the hydrogen-ion concentration of the acid solution would be slightly reduced. This is contrary to the facts. Nevertheless, the precipitation of the tungstic acid on standing suggests that it is colloidal; so also does the fact that if an electrolyte, such as potassium chloride, be included in the sodium tungstate solution, precipitation occurs much more readily on addition of hydrochloric acid.

A series of electrometric titrations was made of solutions to which 25 c.c. of *N*-potassium chloride had been added. The curves obtained were identical with A in Fig. 2, but the solutions began to become cloudy at the stage corresponding approximately with the formation of sodium metatungstate. Table III (col. 2) shows the  $p_H$  values relating to various additions of 0.535*N*-hydrochloric acid to a mixture of 50 c.c. of 0.1*M*-sodium tungstate and 25 c.c. of *N*-potassium chloride: since the amount of acid required for double decomposition is 18.7 c.c., the acid is in excess in every case. The third column, referring to the  $p_H$  values of solutions containing the

TABLE III.

HCl, c.c.	$p_H$ , obs.	$p_H$ , obs. for NaCl + HCl + KCl.	$p_H$ , calc. for Na <sub>2</sub> O, 5WO <sub>3</sub> formation.
20	1.58	2.25	1.56
30	1.23	1.37	1.12
40	1.00	1.14	0.94
50	0.79	0.98	0.83

same amounts of potassium chloride, sodium chloride, and hydrochloric acid, again shows that the tungstic acid solutions possessed enhanced hydrogen-ion concentrations. It should be emphasised that any possible influence caused by the potassium chloride was eliminated by the inclusion of this salt in all these solutions.

(b) *Conductometric method.* The two conductometric titrations detailed in Tables IV and V illustrate the nature of the reaction taking place between sodium tungstate and hydrochloric acid in solutions of different concentrations.

TABLE IV.

100 C.c. of 0.005*M*-Na<sub>2</sub>WO<sub>4</sub> + 5 c.c. of 0.125*M*-NaOH titrated by 0.3247*M*-HCl.

HCl, c.c.	$\kappa \times 10^4$ (obs.), mhos.	Specific conductivities ( $\times 10^4$ ) of solutcs.			$\kappa \times 10^4$ (calc.), mhos.
		Na <sub>2</sub> WO <sub>4</sub> .	NaCl.	HCl.	
0	24.4	10.0	0	—	—
0.5	22.5	9.9	1.9	—	—
1.0	20.5	9.8	3.8	—	—
1.5	18.7	9.7	5.5	—	—
2.0	17.3	9.6	7.3	—	16.9
2.5	17.3	8.0	7.4	—	15.4
3.0	17.3	6.3	10.8	—	17.1
3.5	17.3	4.9	12.4	—	17.3
4.0	17.7	3.0	14.1	—	17.1
4.5	19.6	1.7	15.7	—	17.4
5.0	25.1	0.04	17.3	—	17.3
5.5	30.8	—	17.2	5.4	22.6
6.0	36.1	—	17.1	10.8	27.8
6.5	42.2	—	17.1	16.0	33.1



TABLE V.

100 C.c. of 0.05M-Na<sub>2</sub>WO<sub>4</sub> titrated by 3.247M-HCl.

HCl, c.c. ....	0	0.4	0.8	1.2	1.6	2.0	2.5
$\kappa \times 10^3$ , obs.	8.77	8.77	8.76	8.75	8.75	9.13	10.0
$\kappa \times 10^3$ , calc.	8.60	9.96	9.50	9.80	9.10	9.10	8.9
HCl, c.c. ....	3.0	3.2	3.4	3.6	3.8	4.0	4.4
$\kappa \times 10^3$ , obs.	13.66	15.82	20.00	22.42	24.34	26.52	31.15
$\kappa \times 10^3$ , calc.	8.95	9.60	12.00	14.30	16.60	18.90	23.3

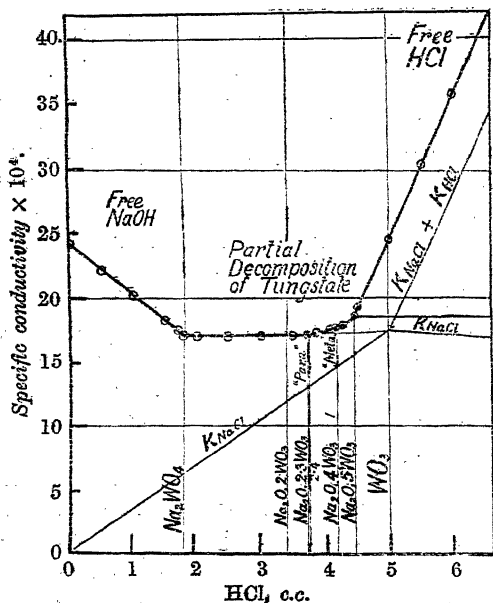
The curve illustrating Table IV is given in Fig. 3, and is seen to be in harmony with the potentiometric curves given in the previous paper and in Fig. 2 of the present paper. The sharp break at 1.93 c.c. corresponds with the neutralisation of the free alkali. Afterwards the conductivity does not begin to change appreciably until sufficient acid has been added to form the paratungstate in solution, whereupon a somewhat gradual increase occurs until 4.35 c.c. of acid have been added. At this point a sharp rectilinear increase in conductivity begins, and passes through the theoretical end-point at 5.01 c.c., *i.e.*, when the additional 3.08 c.c. calculated for the conversion of the sodium tungstate into sodium chloride have been added. The data in Table V give a similar curve.

An attempt has been made to analyse these conductometric-titration curves on the assumption that the observed specific conductivity of a solution at any point in a titration is equal to the sum of the specific conductivities of the solutes at the dilutions in which they are present. For the purpose of calculation, the reaction between sodium tungstate and hydrochloric acid was regarded as taking place according to the equation on p. 1250, and the liberated tungstic oxide was assumed to contribute no conductivity to the solution. The data for sodium tungstate were extrapolated from the records of Walden (*Z. physikal. Chem.*, 1887, 1, 529), and those for sodium chloride and hydrochloric acid from the data given in Landolt-Bornstein's "Tabellen." Tables IV and V give the calculated values of the specific conductivities so obtained. Table IV shows a satisfactory agreement between the calculated and observed values over the range of 2—4 c.c. of added acid; thereafter the observed values are considerably higher than those calculated on the assumption that free hydrochloric acid was present in the solution only after 5.01 c.c. had reacted. The character of the curve in Fig. 3 indicates that the free acid must have existed before that point, actually from 4.35 c.c. If this were so, it would appear that the sodium polytungstate formed at this stage behaved as if it were the salt of a strong acid and therefore was not decomposed by hydrochloric acid. Such a possibility is not easily reconciled with the  $p_H$  values of tungstic acid sols. Similar conclusions may be drawn from

Table V, although it will be observed that, corresponding with additions of acid up to 2.0 c.c., the differences between the observed and calculated specific conductivities of these more concentrated solutions are somewhat greater than in Table IV. Although the theoretical end-point in this case is at 3.08 c.c., the considerable discrepancies appeared at 2.5 c.c.

It may be argued, that, in the first stages of these titrations, the tungstic acid immediately combines with the undecomposed sodium tungstate to form a polytungstate. This appears to be the case, at

FIG. 3.



any rate until the solute has acquired the composition of sodium metatungstate ( $\text{Na}_2\text{O}_4\text{WO}_3$ ), as may be seen from Table VI. This table gives the specific conductivities ( $\kappa \times 10^3$ ) of solutions of sodium tungstate, paratungstate, and metatungstate at various dilutions as calculated from the data of Walden (*loc. cit.*), Rosenheim (*Z. anorg. Chem.*, 1916, **96**, 139), and Soboleff (*ibid.*, 1896, **12**, 16) respectively. The dilutions refer to the volumes in litres containing 1 g.-atom of sodium.

TABLE VI.

Dilution.	32.	64.	128.	256.	512.	1024.
Normal tungstate .....	2.80	1.49	0.78	0.40	0.21	0.11
Paratungstate .....	2.14	1.25	0.70	0.39	0.21	0.12
Metatungstate .....	2.80	1.54	0.84	0.46	0.24	0.13

These figures reveal that the introduction of tungstic acid into a solution of sodium tungstate results in a comparatively small change in conductivity, probably owing to the ionisation of the polytungstates being similar to that of the normal tungstate, thus:  $\text{Na}_2[\text{O}(\text{WO}_3)_x] \rightleftharpoons 2\text{Na}^+ + [\text{O}(\text{WO}_3)_x]^-$ . It appears probable, in view of inflexions in the potentiometric and conductometric curves occurring when approximately 1.5 mols. of hydrochloric acid have been added to 1 mol. of sodium tungstate, in which case  $x = 4$ , that a polytungstate is formed very soon afterwards which behaves as a salt of a strong acid, and therefore resists reaction with further hydrochloric acid and thus remains in solution as such, imparting increased hydrogen-ion concentration and specific conductivity to the solution. Such a view seems feasible when it is remembered that tungstic acid sols, prepared by the prolonged dialysis of solutions of sodium tungstate to which an excess of hydrochloric acid has been added, contain an appreciable amount of sodium oxide (compare Graham, *Proc. Roy. Soc.*, 1864, **13**, 340; Sabanéeff, *Z. anorg. Chem.*, 1897, **14**, 354; Biltz and Vegesack, *Z. physikal. Chem.*, 1910, **68**, 376). If it be assumed that such a sodium polytungstate is formed in these conductometric titrations at the points at which the sudden increases in conductivity begin, viz., at 4.35 c.c. in the first titration and 2.42 c.c. in the second, and that the conductivities then prevailing remain constant as far as the complex tungstate and sodium chloride in the solution are concerned, then the increases in conductivity caused by subsequent additions of hydrochloric acid will be due entirely to the added acid. It happens that in both cases the complex tungstate formed at this stage corresponds with  $\text{Na}_2\text{O}, 5\text{WO}_3$ . It will be seen from Fig. 3 that the specific conductivity due to it and the sodium chloride is  $17.4 \times 10^{-4}$  mho. To test this view, the specific conductivities of the supposed excesses of hydrochloric acid in the various dilutions were calculated and added to the observed conductivity at the point when the limiting complex tungstate was considered to be formed. Table VII, giving

TABLE VII.

Titration.	HCl, c.c.	Dilution of HCl (litres).	Specific conductivity $\times 10^3$ ,	
			obs.	calc.
I	5.0	521	2.51	2.61
	5.5	296	3.07	3.20
	6.0	207	3.61	3.78
	6.5	160	4.22	4.35
	7.5	110	5.09	5.48
II	3.4	35.4	20.0	20.5
	3.8	24.6	24.3	25.0
	4.2	18.9	28.6	29.4
	4.4	16.9	31.2	31.5

the observed and calculated conductivities of the acid solutions in the two titrations, supports this hypothesis.

It was decided to test whether this idea would account for the increased acidity of solutions of sodium tungstate to which an excess of hydrochloric acid had been added. If the complex  $\text{Na}_2\text{O}_5\text{WO}_3$  were formed in the course of the potentiometric titration (Fig. 2), then the amount of acid added in excess of 36.5 c.c. would determine the hydrogen-ion concentration. The following table has been compiled on this basis, it being assumed that the hydrochloric was completely ionised.

HCl, c.c. ....	40.0	50.0	60.0	70.0	80.0
$p_{\text{H}}$ , obs. ....	2.49	2.00	1.77	1.67	1.58
$p_{\text{H}}$ , calc. ....	2.37	1.83	1.63	1.51	1.44

The agreement is not entirely satisfactory, although comparison with the data given in the third column of Table II shows that the hypothesis accounts for much of the increased hydrogen-ion concentration. It also explains the difference in  $p_{\text{H}}$  found in the potassium chloride experiments (see Table III).

Boiling and ageing of acid tungstate solutions had no effect on their specific conductivity, but had slight effects on those solutions in which insufficient acid had been added to form the complex. This is in accordance with the  $p_{\text{H}}$  observations.

*Reaction between Sodium Tungstate and Weak Acids.*—As typical acids, phenylacetic and acetic were chosen, but since the published values of the dissociation constant of the former acid had been obtained from conductivity data, it was considered advisable to redetermine its value at 18° by means of the hydrogen electrode.

NaOH, c.c. ...	7.5	12.5	15.0	20.0	23.0	25.0	27.5
$p_{\text{H}}$ .....	3.73	4.04	4.18	4.45	4.68	4.78	4.95
$K_a \times 10^5$ .....	5.51	5.48	5.44	5.34	5.38	5.54	5.30

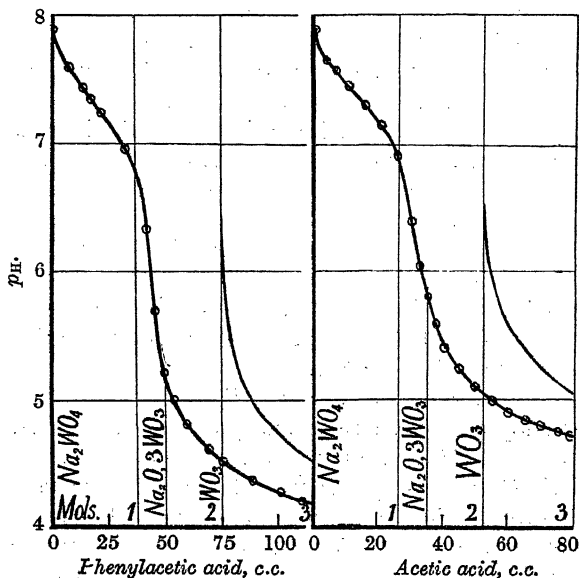
Mean  $K_a = 5.4 \times 10^{-5}$ .

The following  $p_{\text{H}}$  values of various points on the titration curve of 50 c.c. of 0.0667*N*-phenylacetic acid with 0.0980*N*-sodium hydroxide were confirmed by the *E.M.F.* obtained with the quinhydrone electrode. Previous values at 25° range from 5.0—5.45  $\times 10^{-5}$  (Ostwald, *Z. physikal. Chem.*, 1889, 3, 369; Dittrich, *J. pr. Chem.*, 1896, 53, 368; White and Jones, *J. Amer. Chem. Soc.*, 1910, 44, 197).

Fig. 4 gives the titration curves of 50 c.c. of 0.05*M*-sodium tungstate solution with 0.0667*N*-phenylacetic acid and with 0.0936*N*-acetic acid solution. The upper curves represent the  $p_{\text{H}}$  values which would have been established if the sodium tungstate had been entirely converted into the sodium salts of the weak acids

when the stoichiometric amount of the respective acids had been added, and if, thereafter, the curves represented the  $p_H$  values of weak acid solutions buffered by the sodium salts, it being assumed as before that the tungstic acid set free had no effect on their hydrogen-ion concentrations. It is seen that the initial parts of the curves indicate a buffered action in the same  $p_H$  zone as when hydrochloric acid was used. The lower  $p_H$  values assumed by the two solutions soon after 1 equiv. of acid had reacted prove that, some time before the 2 mols. of weak acid had been added, a sodium polytungstate must have been formed which behaved as the salt of strong acid

FIG. 4.



and was in consequence undecomposable by weak acids. If it be considered that this particular sodium polytungstate is formed very soon after the inflexions have occurred, say at 50 c.c. ( $\equiv 1.33$  equivs.) of phenylacetic acid, and 35.6 c.c. ( $\equiv 1.33$  equivs.) of acetic acid, then it is easy to calculate what  $p_H$  values would be set up by the added acids in the presence of the amounts of salts of the respective weak acids formed in the production of the complex tungstate. Tables VIII and IX give (1) the  $p_H$  values of the acid solutions in the two titrations, (2) those which would have been set up if the sodium tungstate had been completely decomposed, liberating tungstic oxide, and (3) those calculated on the basis that the polytungstate formed which resisted the attack of these acids was  $\text{Na}_2\text{O}, 3\text{WO}_3$ .

TABLE VIII.

Phenylacetic acid;  $K_a=5.4 \times 10^{-5}$ .

Acid, c.c.	$p_H$ (1).	$p_H$ (2).	$p_H$ (3).
60	4.81	—	4.97
70	4.59	—	4.67
80	4.46	5.49	4.49
90	4.35	4.97	4.36
100	4.26	4.74	4.27
110	4.20	4.59	4.19
120	4.11	4.48	4.12

TABLE IX.

Acetic acid;  $K_a=1.8 \times 10^{-5}$ .

Acid, c.c.	$p_H$ (1).	$p_H$ (2).	$p_H$ (3).
50	5.11	—	5.14
60	4.91	5.65	4.91
70	4.79	5.25	4.76
80	4.68	5.05	4.65
90	4.65	4.91	4.56
100	4.56	4.80	4.49

In both tables the figures given in the second and fourth columns are in remarkably good agreement. It is fairly certain, therefore, that the cause of the non-precipitation of tungstic oxide from dilute acid solutions is to be traced to the existence of sodium polytungstate, probably in the form of a colloidal electrolyte, *e.g.*,  $2Na^+ + [O(WO_3)_x]^{x-}$ , in which the anion contains much tungstic oxide that is perhaps in a molecularly polymerised form, or, more probably, in a negatively charged colloidal micelle. One difference between the action of a strong and a weak acid lies in the extent to which the normal tungstate is decomposed before it can exist in a solution containing an excess of an acid. When hydrochloric acid was used, the polytungstate shown to be present in acid solution had approximately the composition  $Na_2O, 5WO_3$ , whereas that present in solutions of the weak acids corresponded to  $Na_2O, 3WO_3$ . Much less decomposition had thus occurred.

These observations throw much light on the methods which have been adopted to prepare various polytungstates. Thus, Lefort (*Compt. rend.*, 1876, 82, 1182; *Ann. Chim. Phys.*, 1876, 9, 98) prepared  $Na_2O, 3WO_3, 4H_2O$  by crystallising an aqueous solution of the precipitate obtained by pouring a solution of sodium tungstate into one of boiling acetic acid. Wells (*J. Amer. Chem. Soc.*, 1907, 29, 112) and Gibbs (*Proc. Amer. Acad.*, 1880, 15, 1) both obtained  $Na_2O, 2.5WO_3$  from cold acetic acid solutions of sodium tungstate. By the use of solutions of strong acids (hydrochloric and nitric), substances considerably richer in tungstic oxide have been prepared. According to Ullik (*Sitzungsber. Wien Akad.*, 1867, 56, 157; *J. pr. Chem.*, 1868, 103, 147) and Leontowitsch (*J. Russ. Phys. Chem. Soc.*, 1905, 37, 130) respectively,  $Na_2O, 8WO_3, 12H_2O$  and  $Na_2O, 6WO_3, 15H_2O$  may thus be prepared. The fact that these polytungstates may be obtained from acid solutions furnishes remarkable support to the conclusions drawn from the foregoing experiments.

It was suggested on p. 1257 that the sodium polytungstates containing more tungstic oxide than the metatungstate behaved as if they were the salts of a strong acid, in that they were not easily decomposed by hydrochloric acid. The mode of ionisation of such

an acid cannot be confirmed by direct experiment on account of the insolubility of tungstic oxide. Dumanski, Buntin, Dijatschkovski, and Kniga (*Kolloid-Z.*, 1926, **38**, 208) studied the reaction between sodium tungstate and hydrochloric acid by means of conductivity and cryoscopic measurements. They considered that the rapid increase in conductivity and the abnormal depression of the freezing points (greater than would have been expected if colloidal tungstic acid had been liberated), which occurred after approximately 1.4 equivs. of hydrochloric acid had been added, indicated that tungstic acid was being set free as an ionised semi-colloid. Although this interpretation at first sight may appear to be convincing, it is felt that the hypothesis now advanced is the true one, especially as it affords an explanation of the methods adopted to prepare various polytungstates having high acid content.

The  $p_H$  values of Kargin's (*loc. cit.*) tungstic acid hydrosols do not give any indication of dissociation of the order that would be necessary to impart to the solution the conductivity observed. It appears probable, on the basis of observations described in this paper, coupled with those of Sabanéeff (*loc. cit.*) and Biltz and Vege-sack (*loc. cit.*), that dialysis, even when prolonged, does not cause all the sodium to be removed from the colloidal solution, that Kargin's tungstic acid hydrosols contained a little sodium, and that this sodium was positively charged and the tungstic acid was present as a negatively charged micelle. If the structure and stability of tungstic acid sols, prepared by dialysis of acidified solutions of sodium tungstate, can thus be accounted for, then it appears that the  $p_H$  values of such sols are caused by the hydrogen-ion concentration of the sodium polytungstate they contain.

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## CLXII.—*Physicochemical Studies of Complex Acids.* *Part II. Vanadic Acid.*

By HUBERT THOMAS STANLEY BRITTON and ROBERT ANTHONY ROBINSON.

A NUMBER of alkali-metal vanadates have been described and have generally been prepared either by fusion of carbonates with vanadium pentoxide or by crystallisation of solutions containing various

amounts of acid or alkali. Vanadates are said to exist having the general formula  $n\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ , where  $n = 3, 2, 1, \frac{5}{8}, \frac{4}{7}, \frac{3}{5}, \frac{3}{7}, \frac{2}{5}, \frac{1}{5}$ , etc. Nevertheless, little work has been done on the constitution of alkali vanadates in solution, the most comprehensive investigation being that of Düllberg (*Z. physikal. Chem.*, 1903, 45, 129), who studied the conductometric titration of sodium orthovanadate solutions with hydrochloric acid under various conditions, determined the freezing-point depressions of different vanadate solutions, and postulated the existence in solution of a hexavanadic acid,  $\text{H}_4\text{V}_6\text{O}_{17}$ .

Since the addition of the slightest quantity of acid to a sodium orthovanadate solution produces a yellow coloration, it is interesting to note that while the ortho-, pyro-, and meta-salts are white or a faint yellow, the higher vanadates are orange or red. Thus,  $\text{Na}_2\text{O} \cdot 2\text{V}_2\text{O}_5 \cdot 9\text{H}_2\text{O}$  has been obtained in orange-red crystals (von Hauer, *Sitzungsber. Akad. Wien*, 1856, 21, 337; 1860, 39, 455), and on being heated on the water-bath gives the metavanadate and  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$  (Norblad, *Acta Lund Univ.*, 1874, 2, 1). Norblad also isolated orange-red crystals of  $2\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$ , which Rammelsberg (*Wied. Ann.*, 1883, 20, 938) obtained with  $16\text{H}_2\text{O}$ .

Conductometric and potentiometric titrations of sodium vanadates and vanadic acid are now described, and the results are explained on the hypothesis that vanadium tends to form a heavy molecule, on the border-line between a true solute and a colloidal micelle, and corresponding to  $\text{Na}_2\text{O} \cdot 2\text{V}_2\text{O}_5$  or  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ .

## EXPERIMENTAL.

*Nomenclature.*—There is considerable confusion as to a suitable nomenclature for the large number of compounds of the alkali oxides with vanadium pentoxide. The use of the prefixes "ortho," "pyro," and "meta" for three of the vanadates stresses a false analogy between them and the phosphates and, moreover, tends to single out three of the vanadates from others of equal or greater importance. We therefore propose in this and succeeding communications to designate an alkali vanadate by a prefix denoting the ratio of  $\text{M}_2\text{O}$  to  $\text{V}_2\text{O}_5$  ( $\text{M}$  = alkali metal); thus sodium orthovanadate becomes the 3:1-vanadate, the pyro-salt becomes the 2:1-vanadate, and the compound  $\text{Na}_2\text{O} \cdot 2\text{V}_2\text{O}_5$  will be called the 1:2-vanadate.

### A. Conductometric Titrations.

1. *Direct Titration of Sodium 3:1-Vanadate.*—Vanadium pentoxide dissolves slowly in cold sodium hydroxide solution giving a clear yellow solution, whose colour disappears on standing for some time. If, however, the pentoxide be dissolved in boiling sodium



hydroxide solution, a clear colourless solution is immediately obtained. Such a solution may also be prepared by treating ammonium metavanadate with hot sodium hydroxide solution. In view of the different appearance of the solutions obtained by various methods of preparation, it was of interest to see if the behaviour of the vanadate solutions towards hydrochloric acid could be in any way correlated with their method of preparation.

For this purpose solutions of the sodium 3:1-vanadate were prepared in the following ways and titrated conductometrically with hydrochloric acid at 25°: (1) Ammonium metavanadate,  $\text{NH}_4\text{VO}_3$ , was boiled with the stoichiometrical quantity of sodium hydroxide solution, a current of carbon dioxide-free air being drawn through the solution. (2) Vanadium pentoxide was boiled with the calculated amount of sodium hydroxide solution. Both these solutions were colourless. (3) Vanadium pentoxide was dissolved in the same amount of cold sodium hydroxide solution; this solution was yellow. (4) Solution (3) was kept for 48 hours, and had then become colourless. In all cases, the solutions were 0.005*M* with respect to  $\text{Na}_3\text{VO}_4$ . Solutions (1) and (2) were titrated directly with 0.1*N*-, and (3) and (4) with 0.0933*N*-hydrochloric acid, the liberation of the vanadic acid according to the equation  $2\text{Na}_3\text{VO}_4 + 6\text{HCl} \rightarrow \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O} + 6\text{NaCl}$  corresponding to 15.0 c.c. in the first two cases and to 16.1 c.c. in the last two. The specific conductivities,  $\kappa$ , at different titres are given in Table I.

TABLE I.

*Specific conductivities ( $\kappa \times 10^3$ ) of 100 c.c. of 0.005*M*- $\text{Na}_3\text{VO}_4$  prepared in different ways and titrated directly with HCl.*

	$\text{Na}_2\text{O} : \text{V}_2\text{O}_5 =$	3:1	2.5:1	2:1	1.5:1	1:1	0.5:1	0.25:1	0:1
Soln. 1 .....		2.14	1.92	1.72	1.58	1.54	1.58	1.73	1.98
„ 2 .....		2.13	1.92	1.73	1.57	1.53	1.58	1.73	2.01
„ 3 .....		2.14	1.93	1.74	1.56	1.52	1.61	1.78	2.06
„ 4 .....		2.09	1.88	1.68	1.53	1.49	1.54	1.75	2.00

*Continuation of titration of Solution 2 beyond liberation of vanadic acid at 15 c.c. of HCl:*

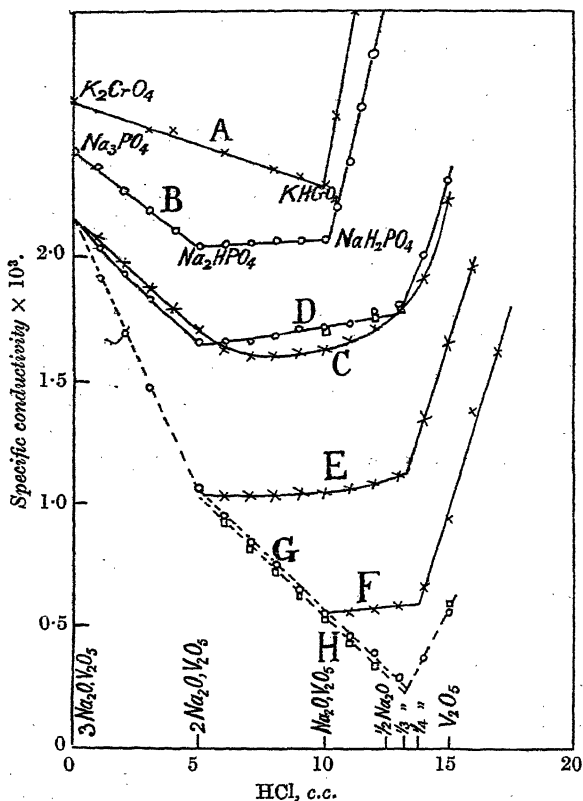
HCl, c.c. ...	15	16	17	18	19	20	21	22	23	24	25
$\kappa \times 10^3$ .....	2.01	2.20	2.46	2.74	2.97	3.19	3.45	3.68	3.91	4.14	4.34

Table I indicates that all the vanadate solutions reacted with hydrochloric acid in the same way, irrespective of the manner in which they were prepared. The small differences between the conductivities of Solutions 3 and 4 may perhaps be ascribed to the disappearance of the yellow colour on ageing. When the results

are plotted, curves are obtained very similar to Curve C (Fig. 1), which will be discussed later.

2. *Effects of Ageing and Boiling.*—In view of the remarkable observation of Düllberg (*loc. cit.*), that the conductivity of solutions of sodium 3:1-vanadate, to which varying quantities of hydrochloric acid had been added, underwent a change on standing, we

FIG. 1.



have repeated and confirmed his experiments. In addition, we have investigated the effect of boiling such solutions. Three series of experiments were performed; a series of solutions, 100 c.c. in volume and 0.005*M* with respect to  $\text{Na}_3\text{VO}_4$ , were prepared containing 0.1*N*-hydrochloric acid in various quantities from 0 to 15 c.c., and their conductivities were measured (a) immediately, and (b) after they had stood for six days; a similar series of solutions was boiled and the conductivity then measured (c) at 25°.

In all cases, the addition of even the slightest amount of acid to a colourless vanadate solution produced a yellow coloration, which increased in intensity with addition of hydrochloric acid until about half the amount required to liberate  $\text{H}_3\text{VO}_4$  had been added, *i.e.*, 7 or 8 c.c. Boiling the coloured solutions decolorised those containing 10 c.c. of hydrochloric acid or less, and ageing decolorised those containing 8 c.c. or less. The results of these experiments are given in Table II and shown graphically in Fig. 1.

TABLE II.

*Specific conductivities of 100 c.c. of 0.005M- $\text{Na}_3\text{VO}_4$  containing x c.c. of 0.1N-HCl, (a) immediately, (b) after standing for 6 days, (c) boiling, after addition of acid.*

x .....	0	1	2	3	4	5	6	7
$\text{Na}_2\text{O}/\text{V}_2\text{O}_5$ .....	3	2.8	2.6	2.4	2.2	2	1.8	1.6
$\kappa \times 10^8$ (a) .....	2.15	2.08	1.97	1.87	1.79	1.70	1.62	1.58
(b) .....	2.15	2.03	1.93	1.83	—	1.65	1.65	1.65
(c) .....	2.09	2.00	—	1.76	—	—	—	1.64
x .....	8	9	10	11	12	13	14	15
$\text{Na}_2\text{O}/\text{V}_2\text{O}_5$ .....	1.4	1.2	1	0.8	0.6	0.4	0.2	0
$\kappa \times 10^8$ (a) .....	1.60	1.61	1.62	1.67	1.71	—	1.91	2.23
(b) .....	1.68	1.70	1.71	1.73	1.78	1.80	2.01	2.31
(c) .....	—	1.70	1.70	—	1.75	1.78	—	2.30

The results of the first experiment (Curve C) are almost identical with the direct titrations described above, the small difference being due to the dilution of the solution in the course of the former titration. No break appears in the curve corresponding to a 2 : 1- or a 1 : 1-vanadate. The effect of ageing is shown in Curve D. The effect of boiling is almost identical, as will be seen from the data in Table II. A break occurs at a point corresponding with the 2 : 1-vanadate, and another which approximates to the 1 : 3-vanadate. These breaks are shown more clearly by Curve G, constructed by subtracting from the total conductivity of the solution that due to the sodium chloride formed. Thus, Curve G represents the conductivity of the solution due to the vanadate at different points. For comparison, the titration curves of a potassium chromate (A) and a sodium phosphate (B) solution are shown on the same graph, but the scale of the conductivity axis has been moved. Breaks are found in these curves corresponding with  $\text{KHCrO}_4$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{NaH}_2\text{PO}_4$ , and it is evident that the vanadate curves are anomalous.

3. *Titration of the Sodium 1 : 1-Vanadate.*—Curves C and D of Fig. 1 show that the variation of conductivity during titration with hydrochloric acid of a solution corresponding in composition with the 3 : 1-vanadate depends on whether the measurement is made immediately, or after boiling or ageing, after each addition of acid.

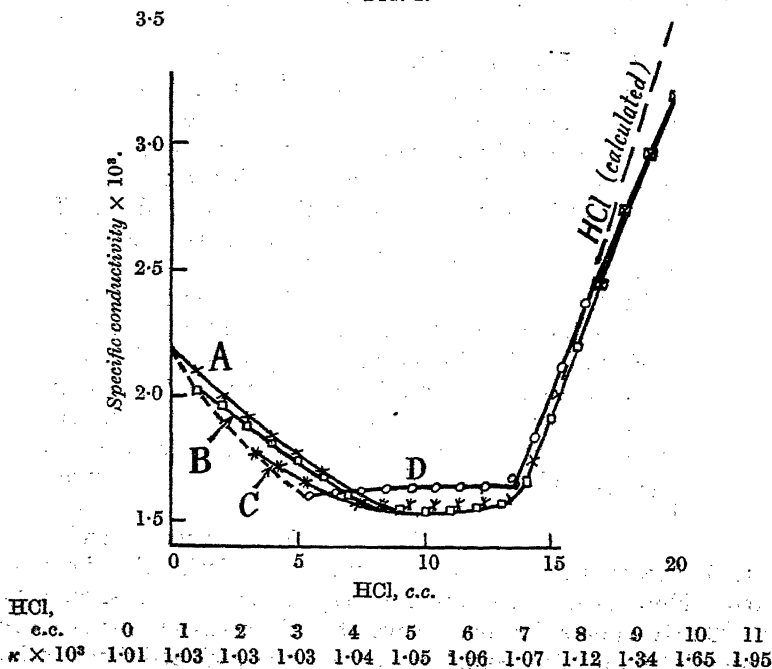
In order to study this matter further, a solution was prepared of the 1:1-vanadate by boiling the pentoxide with the calculated amount of sodium hydroxide solution. The vanadium content was the same as in the previous experiments. 100 C.c. of the solution were then titrated directly with 0.1*N*-hydrochloric acid; the conductivities found were as follows, the corresponding curve being F (Fig. 1), which starts at 10 c.c.:

HCl, c.c. ....	0	1	2	3	4	5	6	7
$\kappa \times 10^3$ .....	0.544	0.550	0.562	0.573	0.657	0.925	1.38	1.61

Since the initial conductivity of this solution is due entirely to the 1:1-vanadate, we should expect it to agree with the conductivity of the corresponding solution in Curve D, after correction has been made for the sodium chloride in the latter. Satisfactory agreement is obtained. Moreover, if from Curve F we subtract the conductivity of the sodium chloride formed during the reaction, a curve is obtained identical with the latter part of Curve G.

4. *Titration of the Sodium 2:1-Vanadate.*—In a similar manner, 100 c.c. of a 0.005*M*-solution corresponding in composition with the 2:1-vanadate ( $\text{Na}_2\text{HVO}_4$ ) were prepared and titrated with 0.1*N*-hydrochloric acid (see Curve E, Fig. 1, starting at 5 c.c.):

FIG. 2.



Again, satisfactory agreement was obtained between the initial conductivity of this solution and that of the solution in Curve D corresponding with 5 c.c. of hydrochloric acid when corrected for the conductivity of its sodium chloride. Also, if correction is made in Curve E for the sodium chloride formed, giving Curve H, the resulting conductivities are only slightly lower than those in Curve G.

Since Curves E and F relate to a direct titration of the 2 : 1- and 1 : 1-vanadate solutions respectively, it would appear that no influence of boiling or ageing on the solutions of Curves D and C should appear beyond the point relating to 5 c.c. of hydrochloric acid. To check this deduction, a solution of 100 c.c. of 0.005*M*- $\text{Na}_3\text{VO}_4$  was treated with sufficient hydrochloric acid to form the 2 : 1-vanadate, and boiled. It was then titrated directly with 0.0933*N*-acid without further boiling on addition of acid. A curve was obtained almost identical with that portion of Curve D beyond 5 c.c. of added acid.

We also showed that a solution of the 2 : 1-vanadate, prepared by dissolving the pentoxide in *cold* sodium hydroxide solution, and titrated directly with hydrochloric acid, gave a curve only slightly lower than Curve E in Fig. 1 and identical with it in form, although, unlike the above, this solution was yellow in colour.

It is therefore concluded that boiling or ageing effects are only to be obtained with solutions less acid than the 2 : 1-vanadate, although the effect of omitting the boiling or ageing operation with such solutions may be apparent in the subsequent titration after the 2 : 1-vanadate stage is passed.

5. *Effects of Boiling on Solutions between the 3 : 1- and the 2 : 1-Vanadate.*—Since boiling or ageing has little or no influence on solutions of the 2 : 1-vanadate, but considerable effect on the 3 : 1-vanadate, an experiment was carried out with solutions intermediate between these two vanadates. To four portions of a solution of the 3 : 1-vanadate,  $x$  c.c. of 0.0933*N*-hydrochloric acid were added, where  $x = 0, 1, 3.25, \text{ and } 5.40$  c.c. respectively. Each solution was boiled, diluted to 100 c.c. and 0.005*M* with respect to the vanadium content, and titrated directly, without any subsequent boiling, with acid of the same concentration.

The conductivities found are shown in Table III and plotted in Fig. 2. The initial broken-line curve corresponds to the boiling effect shown in Curve D in Fig. 1. This experiment shows that initial boiling of solutions between the 3 : 1- and the 2 : 1-vanadate lowers their conductivity, but on direct titration they tend to revert to a curve of the type C of Fig. 1. Initial boiling of a solution corresponding with the 2 : 1-vanadate leads, however, on titration with

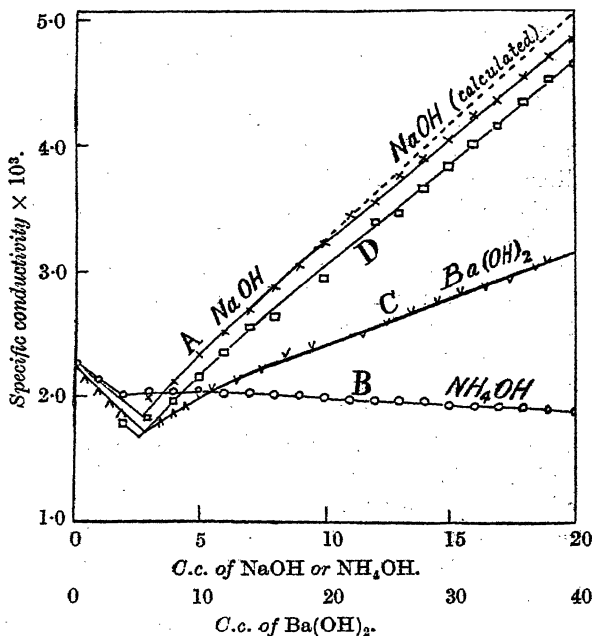
TABLE III.

Specific conductivities of 100 c.c. of (a) 3:1-, (b) 2.8:1-, (c) 2.35:1-, (d) 2:1-vanadate, boiled initially and titrated directly with 0.0933N-HCl.

$\text{Na}_2\text{O}:\text{V}_2\text{O}_5\ldots$	3:1	2.8:1	2.35:1	2:1	1.5:1	1:1	0.5:1	0:1
$\kappa \times 10^3$ (a) .....	2.17	2.10	1.89	1.73	1.55	1.54	1.60	2.21
(b) .....	—	2.02	1.86	1.71	1.56	1.54	1.60	2.21
(c) .....	—	—	1.78	1.64	1.57	1.56	1.62	2.21
(d) .....	—	—	—	1.61	1.62	1.64	1.66	2.30

acid, to a different type of curve, identical in form with Curve D of Fig. 1, which was obtained by boiling the solution after each addition of acid.

FIG. 3.



Alkali, c.c.	0.	2.	4.	6.	10.	15.	19.
$\kappa \times 10^3$ (a) .....	2.30	1.96	2.10	2.50	3.20	4.03	4.70
(b) .....	2.26	2.04	2.04	2.02	1.98	1.93	1.91
(c) .....	2.28	2.05	1.88	1.81	2.01	2.23	2.38
(d) .....	1.78	1.95	2.34	2.61	3.39	4.16	4.84

6. *Titration of Vanadic Acid with Alkalis.*—The effect of hydrochloric acid on vanadate solutions having been determined, the reverse titration of vanadic acid with alkalis was investigated. 0.005M Vanadic acid ( $\text{H}_3\text{VO}_4$ ) was formed by the addition of hydro-

chloric acid to the 3 : 1-vanadate and 100 c.c. were titrated with (a) 0.1*N*-sodium hydroxide, (b) 0.1023*N*-ammonia, and (c) 0.0487 *N*-baryta. Also (d) 100 c.c. of a solution corresponding with the minimum conductivity in Curve G of Fig. 1 (*i.e.*, prepared by diluting a mixture of 13 c.c. of 0.1*N*-hydrochloric acid and 25 c.c. of 0.02*M*- $\text{Na}_3\text{VO}_4$ ) were titrated with 0.1*N*-sodium hydroxide. The conductivities are given above and are plotted in Fig. 3, the Curve D starting from 2 c.c., because 13 c.c. of 0.1*N*-acid were used in making up this solution, whereas 15 c.c. would have been required to give  $\text{H}_3\text{VO}_4$  (see Fig. 1).

The first part of the curve, in all three cases, consists of a sharp drop, corresponding with the neutralisation of some excess acid; in the sodium hydroxide titration, the curve then rises regularly, showing no break which could be attributed to the 1 : 1-, 2 : 1-, or 3 : 1-vanadates.

The slow fall in the ammonium hydroxide curve is to be explained by the gradual dilution of the solution, which is more than sufficient to counterbalance the conductivity due to the ammonium hydroxide added; moreover, the ammonium chloride exerts a buffering effect. The baryta curve resembles that for sodium hydroxide, and a similar explanation applies, although here there is the added complication of a precipitation of a barium vanadate, which appears slowly during the course of the titration.

### B. Potentiometric Titrations.

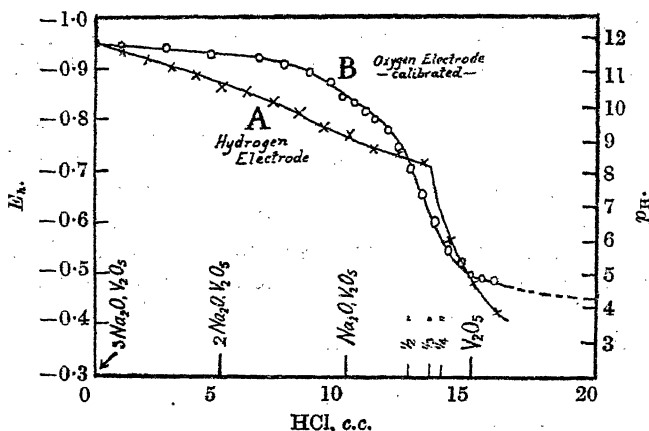
An attempt has been made to follow the course of the titration of sodium 3 : 1-vanadate with hydrochloric acid potentiometrically. In a 0.005*M*- $\text{Na}_3\text{VO}_4$  solution, the hydrogen electrode was found to give steady, reproducible potentials, the *E.M.F.* in eight determinations varying only between -0.948 and -0.950, measured against the normal calomel electrode. This corresponds to  $p_{\text{H}}$  11.65 and  $[\text{OH}'] = 0.0045*N*$ , indicating 30% hydrolysis. The cell used was  $\text{H}_2(\text{Pt})|0.005*M*-\text{Na}_3\text{VO}_4|\text{sat. KCl}|1.0*N*-\text{KCl}, \text{Hg}_2\text{Cl}_2|\text{Hg}$ . On titration of the solution with 0.1*N*-hydrochloric acid, the electrode ceased to give satisfactory results: it showed a slight but steady fall in potential up to 13 c.c., but then became very erratic, the *E.M.F.* falling rapidly. A typical titration is illustrated in Fig. 4. That reduction was proceeding, at any rate in the more acid solutions, was evident from their blue colour after hydrogen had been passing for a short time.

Titration with the oxygen electrode also yielded unsatisfactory results. As is well known, this electrode does not give reproducible readings even under favourable conditions; it was therefore calibrated against the value of -0.950 volt, obtained for the hydrogen

electrode in  $0.005M\text{-Na}_3\text{VO}_4$  solution, and then afforded qualitative results, as may be seen from a typical curve in Fig. 4; in agreement with the hydrogen electrode, there is no sharp fall, but a considerable lowering of the  $p_H$  of the solution in the region of the 1:2-, 1:3-, and 1:4-vanadates.

Attempts were made to use the quinhydrone electrode in the titration of vanadic acid solutions with alkali. Its behaviour was very erratic, however, a fact which is not surprising in view of the closeness of the normal reduction potential of quinone-quinol to that of quinquevalent-quadrivalent vanadium.

FIG. 4.



### Discussion.

The foregoing experiments may be summarised as follows: The sodium 3:1-vanadate, when titrated directly with hydrochloric acid, shows but little analogy with the formally similar phosphate (compare Curves B and C, Fig. 1): while the phosphate shows breaks corresponding with the primary and secondary salts, the vanadate has a continuously varying conductivity, although, when allowance is made for the conductivity due to the sodium chloride in the solution, a break appears at a point corresponding with 13/15ths decomposition. If these solutions are boiled or aged after each addition of acid in the course of the titration, the nature of the curve changes, a break being obtained at the 2:1-vanadate and, according to Düllberg (*loc. cit.*), in the more concentrated solutions, at the 1:1-vanadate. The main divergence from the phosphate analogy, however, lies in the break at 13/15ths decomposition, which appears in all the titrations. These boiling (or ageing)



effects are not operative in all vanadate solutions. Solutions of the 3:1-vanadate, when titrated directly with acid, follow what we may term the "abnormal" smooth curve, typified by C in Fig. 1. If these solutions are boiled after every addition of acid until the 2:1-vanadate is reached, another type of curve, exemplified by D in Fig. 1, which we will call the "normal" type, is obtained. Boiling a solution corresponding to the 2:1-vanadate, or a more acid vanadate, produces no change in its titration with hydrochloric acid. Omission of the boiling operation at any stage previous to the 2:1-vanadate, however, results in the solution reverting to the "abnormal" curve on further titration.

Direct titration by alkali of a solution corresponding with vanadic acid shows no evidence of salt formation corresponding to the 1:1-, 2:1-, or 3:1-vanadates.

Potentiometric titration of the 3:1-vanadate with hydrochloric acid, using the hydrogen electrode, indicates that there is a steady fall in  $p_H$  from 11.65 in the 3:1-vanadate solution to about 8.4 when 13/15ths of the decomposition is complete, after which the solution rapidly becomes acid.

Düllberg explained his titration curves by postulating a hexavanadic acid,  $H_4V_6O_{17}$  (i.e.,  $3V_2O_5 \cdot 2H_2O$ ). At the point corresponding to 12.5/15ths of the decomposition, he supposed that the monohydrogen salt of this acid was formed, viz.,  $HN_3V_6O_{17}$  or  $Na_2O \cdot 2V_2O_5 \cdot \frac{1}{3}H_2O$ , and that the ion  $HV_6O_{17}'''$  did not readily dissociate. In this way he accounted for the decomposition apparently ceasing at 5/6ths of the expected titration.

Against this hypothesis it must be urged that only a small number of vanadates can be derived by simple substitution of hexavanadic acid. Moreover, our figures tend to show that the break occurs somewhat beyond 5/6ths of the decomposition.

By subtracting the conductivity of the sodium chloride from that of the sodium vanadate-sodium chloride mixtures, as in Curves G and H of Fig. 1, an estimate can be made of the minimum conductivity; averaging these values from eight experiments, we estimate this conductivity to be 0.00029 mho, the minimum value occurring at 12.83/15ths of the acid required to liberate vanadic acid; in all cases the solution was 0.005M with respect to vanadium. This is a surprisingly low conductivity, indicating a very heavy molecule, i.e., polymerisation.

A more feasible, and at the same time a more fruitful, hypothesis is to postulate the existence of a complex with a high  $V_2O_5 : Na_2O$  ratio, corresponding with 12.85 c.c. of hydrochloric acid. Such a complex would have the approximate composition  $Na_2O \cdot 2V_2O_5$  or

$\text{Na}_2\text{O}, 3\text{V}_2\text{O}_5$ , but as we shall show that this can only exist in a polymerised form, it would appear to be on the border line between a true solute and a colloidal micelle, and consequently a simple ratio between  $\text{Na}_2\text{O}$  and  $\text{V}_2\text{O}_5$  is not to be expected.

Such a complex could easily give rise to a series of salts by addition of small amounts of acids and evaporation, especially as it is by no means certain that many of these more complex vanadates are of definite chemical composition.

Now, Düllberg has shown that a solution, 0.1*M* with respect to vanadium, and corresponding with 12.5 c.c. of hydrochloric acid in our graph (Fig. 2), has a freezing point of  $-0.0751^\circ$ . For a solution of 0.1*M*- $\frac{1}{4}(\text{Na}_2\text{O}, 2\text{V}_2\text{O}_5)$  we should expect a depression of  $-0.186^\circ$  if the solution were un-ionised; for a doubly polymerised molecule we should expect  $-0.093^\circ$ , and for a trebly polymerised molecule  $-0.0465^\circ$ . The last figure would be somewhat higher if the molecule were ionised, and if it be assumed that our complex contains three atoms of vanadium, the freezing point would indicate about 21% dissociation. Moreover, Düllberg has demonstrated that the 1:1-vanadate is probably trebly polymerised, showing that condensation of molecules is occurring even at this stage of the titration.

In one case (Soln. 2 in Section 1), the conductometric titration of a 0.005*M*-3:1-vanadate solution with hydrochloric acid was carried beyond the liberation of vanadic acid at 15 c.c. of 0.1*N*-acid. The latter portion of this titration, from 15 to 25 c.c. of acid, is shown in Fig. 2, where it is contrasted with the calculated conductivity of the added hydrochloric acid, assumed present as free acid. The observed conductivities at titres of 15 and 25 c.c. were 0.00201 and 0.00434 mho, respectively, a difference of 0.00233 mho. The conductivity due to the addition of 10 c.c. of 0.1*N*-acid is calculated as 0.00320 mho, or, after allowing for the decrease in the conductivity of the sodium chloride on dilution from 115 to 125 c.c., which is approximately 0.00016 mho, the calculated difference becomes 0.00304. The observed increase in conductivity is therefore about 23% less than the calculated, showing that the complex is not entirely resistant to the action of acids, but that some replacement of sodium by hydrogen occurs.

Similar conclusions are to be drawn from the alkali titration of vanadic acid. In Fig. 3 the titration of 0.005*M*-vanadic acid with 0.1*N*-sodium hydroxide is contrasted with the calculated increase in conductivity due to the sodium hydroxide calculated as free alkali. Between the titres of 3 c.c. and 20 c.c. of caustic soda the conductivity increased by 0.00289 mho. The addition of 17 c.c.

of 0.1*N*-sodium hydroxide would give a calculated increase of 0.00333 mho, or 0.00305 mho after 0.00028 mho is allowed for the decrease in conductivity owing to the dilution of the solution from 103 to 120 c.c. The observed increase is, therefore, 5% less than the calculated increase in conductivity, showing that there is a small interaction between the complex and the sodium hydroxide.

The decomposition of sodium 3 : 1-vanadate, when the solution is boiled or aged after each addition of acid, would appear to proceed as follows : The 3 : 1-vanadate is hydrolysed almost completely into sodium hydroxide and the 2 : 1-vanadate; addition of hydrochloric acid neutralises the hydroxide, and at one-third decomposition the solution consists, therefore, of sodium chloride and the 2 : 1-vanadate. The first reaction may be represented as  $\text{NaOH} + \text{Na}_2\text{HVO}_4 \longrightarrow \text{NaCl} + \text{Na}_2\text{HVO}_4$ . Now in Expt. B of Section 2 we found that the conductivity at one-third decomposition was 0.00165 mho, of which 0.000585 mho was due to sodium chloride. Thus the conductivity of the 2 : 1-vanadate is 0.001065 mho, and, adding to this the conductivity of an equimolecular amount of sodium hydroxide, *viz.*, 0.001175 mho, we get 0.00224 mho for the calculated value of the conductivity of the 3 : 1-vanadate, compared with 0.00215 mho for the observed. The discrepancy is probably due in the first place to the hydrolysis of the 3 : 1-vanadate being not quite complete, and secondly, to the 2 : 1-vanadate being itself hydrolysed to some extent.

The next stage, between one-third and two-thirds decomposition, consists of the formation of a condensed 1 : 1-vanadate :  $3\text{Na}_2\text{HVO}_4 + 3\text{HCl} \longrightarrow \text{Na}_3\text{V}_3\text{O}_9 + 3\text{NaCl} + 3\text{H}_2\text{O}$ . Further addition of acid results in an abstraction of soda from this heavy 1 : 1-vanadate molecule until a ratio of Na : V between 1 : 2 and 1 : 3 is reached, whereupon the molecule becomes sufficiently stable, and the residual soda is so closely bound in the complex that further addition of the acid causes no change, or only a very gradual and partial replacement. No break appears at two-thirds neutralisation, where the 1 : 1-vanadate begins to be converted into the complex, but this is marked by the fact that solutions containing the complex cannot be decolorised by boiling.

In the case of direct titration of the 2 : 1- or 1 : 1-vanadates, the same sequence of changes occurs.

The potentiometric curves given in Fig. 4, though by no means satisfactory, explain why Rosenheim and Yang (*Z. anorg. Chem.*, 1923, **129**, 181) found that, on titration of solutions of the 3 : 1-vanadate with sulphuric acid, phenolphthalein became decolorised when approximately 2 equivs. of acid had been added. The curves

show that the solutions are buffered at this stage so that the change-point could not possibly be sharp.

The same problem has been approached in another direction by Dumanski (*J. Russ. Phys. Chem. Soc.*, 1924, 54, 703), who prepared vanadium pentoxide sols by the method of Biltz (*Ber.*, 1904, 37, 1095), *i.e.*, grinding ammonium metavanadate with hydrochloric acid, filtering off the residue, and shaking it with water. On dilution of the red solution, a yellow solution was obtained, having a higher electrical conductivity and having no particles visible in the ultra-microscope. On coagulation with barium chloride, a small amount of barium was absorbed, increasing to a constant value after several hours' standing, whereupon the solid approximated to the composition  $\text{BaH}_2\text{V}_6\text{O}_{17}$ . The conductivity of the solution increased at the same time, consistent with a replacement of barium ions by hydrogen ions. From the amount absorbed in the first stage, the formula  $[\text{H}_2\text{V}_6\text{O}_{17}(\text{V}_2\text{O}_5)_6]'' + 2\text{H}^+$  was deduced.

The authors wish to thank the Chemical Society for a grant from the Research Fund.

UNIVERSITY COLLEGE, EXETER.

[Received, April 16th, 1930.]

## NOTES.

*The Supposed Mandelonitrile.* By WILSON BAKER and RANDAL GEORGE ARTHUR NEW.

WOOD and LILLEY (J., 1925, 127, 95) have described the spontaneous transformation of mandelonitrile to a "yellow solid," m. p.  $196^\circ$  (corr.), stated to be mandelonitrile. They claim to have confirmed the isonitrile structure by determinations of the molecular weight and of the percentage of nitrogen, by reduction to the base  $\text{CHPh}(\text{OH})\cdot\text{NH}\cdot\text{CH}_3$  (I) (yellowish-grey solid, m. p.  $180^\circ$  decomp.), and also by acid hydrolysis giving benzaldehyde, formic acid, tarry matter and mandelic acid. It is very unlikely that the change nitrile  $\rightarrow$  isonitrile should occur, and the high melting points of Wood and Lilley's products are not consistent with the structures given. Further the base (I) spontaneously loses water, giving the Schiff's base  $\text{CHPh}\cdot\text{N}\cdot\text{CH}_3$  (Zaunschirm, *Annalen*, 1888, 245, 281). We have found that the pure substance, crystallised twice from alcohol and twice from benzene, melts at  $198^\circ$  and has the formula  $\text{C}_{23}\text{H}_{18}\text{O}_2\text{N}_2$  (Found: C, 77.7; H, 5.1; N, 7.6; *M*, by Rast's method, 372. Calc.: C, 78.0; H, 5.1; N, 7.9%; *M*, 354), and that it is rapidly and completely hydrolysed by dilute acids, giving

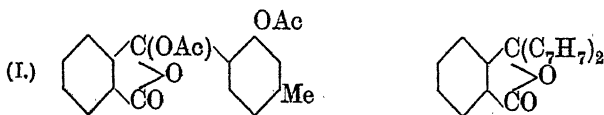
benzaldehyde (1 mol.), mandelic acid (2 mols.), and ammonia (2 mols.).

Examination of the literature showed that this substance,  $C_{23}H_{18}O_2N_2$ , was first obtained from bitter-almond oil and described by Laurent in 1835 under the name "benzimide" (*Ann. Chim. Phys.*, [2], 59, 398; see also Laurent, *ibid.*, 1835, [2], 60, 218; *Annalen*, 1836, 17, 89; *Ann. Chim. Phys.*, 1837, [2], 66, 194; *Berzelius' Jahresber.*, 1837, 16, 246). Zinin in 1840 (*Annalen*, 34, 188; see also *Berzelius' Jahresber.*, 1842, 21, 356) and Gregory in 1845 (*Annalen*, 54, 372) prepared it from bitter-almond oil and potassium cyanide, and both assigned to it the correct molecular formula. It is clear that Gregory prepared it as early as 1834, but did not examine it till later. Laurent and Gerhardt (*Jahresber.*, 1850, 488) realised the identity of "benzimide" with Zinin and Gregory's product. Later Zinin showed (*J. Russ. Chem. Soc.*, 1869, 1, 213; see *Ber.*, 1869, 2, 509, 552) that the substance could be hydrolysed by acid to benzaldehyde, mandelic acid, and ammonia. The compound was first recognised as the acetal of benzaldehyde and mandelonitrile — di-( $\alpha$ -cyanobenzyloxy)phenylmethane,  $CHPh[O\cdot CH(CN)Ph]_2$ —by Schiff in 1870 (*Annalen*, 154, 346). The same conclusion was reached as the result of careful work and rational syntheses by Stollé (*Ber.*, 1902, 35, 1590) and later by Savelsberg (*J. pr. Chem.*, 1916, 93, 271), the latter having acknowledged Stollé's priority (*ibid.*, 1917, 96, 186). A correction of Wood and Lilley's work (Stollé, *Ber.*, 1925, 58, 975) appears to have been overlooked (see, for example, "Organic Syntheses," Vol. 6, 60) and we desire to record our complete agreement with the work of Stollé and Savelsberg.—THE DYSON PERRINS LABORATORY, OXFORD. [Received, April 5th, 1930.]

*Syntheses of 1-Methylanthraquinones.* By ARTHUR FAIRBOURNE  
and GRAHAM EDWARD FOSTER.

IN an attempt to obtain a sample of 1:2-dimethylantraquinone, by a process which should ensure its being free from the difficultly separable 2:3-isomeride (J., 1921, 119, 1573), 4-hydroxy-1:2-dimethylantraquinone was prepared (J., 1923, 123, 1137). The intermediate 2-*o*-hydroxyxyloylbenzoic acid, with acetic anhydride and sodium acetate, has yielded colourless plates, m. p. 195° (Found: C, 67.5; H, 5.1; *M*, 360.  $C_{20}H_{18}O_6$  requires C, 67.8; H, 5.1%; *M*, 354). Since it was stable towards hot water, this *diacetate* presumably has the structure (I) (compare Gleason and Dougherty, *J. Amer. Chem. Soc.*, 1929, 51, 310). The *hydroxyanthraquinone* has similarly been acetylated to yield 4-acetoxy-1:2-dimethylantraquinone, yellow

needles from alcohol, m. p.  $154^{\circ}$  (Found : C, 73.5; H, 4.9.  $C_{18}H_{14}O_4$  requires C, 73.5; H, 4.8%), but could not successfully be reduced in either acid or alkaline media (compare Elbs, *J. pr. Chem.*, 1890, **41**, 1; Braun and Bayer, *Ber.*, 1926, **59**, 914); distillation over zinc dust produced a colourless crystalline sublimate, m. p.  $200^{\circ}$ , which cannot have been the unknown 1:2-dimethylantracene since it was oxidisable to a product melting at  $280^{\circ}$  (compare Birukoff, *Ber.*, 1887, **20**, 2068; Fischer and Sapper, *J. pr. Chem.*, 1911, **83**, 201).



The proposed method of Pickles and Weizmann (P., 1904, **20**, 201) for synthesising anthraquinones of proved structures from the corresponding Grignard reagents and phthalic anhydride is likely to be particularly applicable when 1-methylantraquinones are required, but appears never to have been adopted for that purpose, owing to a fear that simultaneous formation of diarylphthalides (as II) would render it unsuitable. Opportunity for synthesising 1:2-dimethylantraquinone from magnesium *o*-3-xylyl bromide has not occurred, but the method has been tested in the similar case of magnesium *o*-tolyl bromide, under conditions maintaining a continuous excess of the anhydride to minimise further reaction of 2-*o*-toluoylbenzoic acid. The latter crystallised from alcohol in colourless needles, m. p. above  $120^{\circ}$  (Found : equiv. by titration with *N*/10-baryta, 236.  $C_{15}H_{12}O_3$  requires equiv., 240), and was converted into 1-methylantraquinone, m. p.  $173^{\circ}$ , agreeing with the description of Fischer and Sapper (*loc. cit.*) of a specimen synthesised in a different manner (Found : C, 81.0; H, 4.4. Calc. : C, 81.1; H, 4.5%). The method thus renders possible reaction (c) (J., 1921, **119**, 1574) which could not previously be realised.

The authors are indebted to the Chemical Society for a grant which has partly met the expenses incurred in this work, and also to the Department of Scientific and Industrial Research for a maintenance grant to one of them.—KING'S COLLEGE, LONDON. [Received, November 7th, 1929.]

CLXIII.—*A Revision of the Atomic Weight of Tantalum. Determination of the Ratios  $\text{TaBr}_5 : 5\text{Ag} : 5\text{AgBr}$  and  $\text{TaCl}_5 : 5\text{Ag} : 5\text{AgCl}$ .*

By KOLAR RAMAKRISHNAIYER KRISHNASWAMI.

THE accepted value for the atomic weight of tantalum is based on results which are not in satisfactory agreement. Marignac (*Arch. Sci. phys. nat.*, 1866, 26, 89), who was the first to employ purified materials, used the double fluorides of tantalum with potassium and with ammonium,  $\text{R}_2\text{TaF}_7$ , to determine the ratios  $2\text{K}_2\text{TaF}_7 : \text{Ta}_2\text{O}_5$ ,  $\text{K}_2\text{TaF}_7 : \text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4 : \text{Ta}_2\text{O}_5$ , and  $2(\text{NH}_4)_2\text{TaF}_7 : \text{Ta}_2\text{O}_5$ , and calculated therefrom values which ranged from 182.66 to 183.55, giving as a mean,  $\text{Ta} = 182.98$ . Hinrichson and Sahlbom (*Ber.*, 1906, 39, 2600) carried out five determinations of the ratio  $2\text{Ta} : \text{Ta}_2\text{O}_5$  by observing the gain in weight of known amounts of the metal when heated in a stream of oxygen; values ranging from 180.60 to 181.72 were obtained for Ta, the mean being  $181.02 \pm 0.09$ . Van Haagen (Thesis, University of Pennsylvania, 1909) sought to fix the ratio  $2\text{TaBr}_5 : \text{Ta}_2\text{O}_5$  by weighing the pentoxide formed from the hydrolysis of a known weight of the pentabromide; eight determinations gave values ranging from 183.10 to 183.42, the mean being  $183.28 \pm 0.09$ . Chapin and Smith (*J. Amer. Chem. Soc.*, 1911, 33, 1497) redetermined the ratio  $2\text{TaBr}_5 : \text{Ta}_2\text{O}_5$ , and calculated  $\text{Ta} = 181.69$ — $181.94$ ; mean  $181.82 \pm 0.04$ . Balke (*ibid.*, 1910, 32, 1127) conducted eight determinations of the ratio  $2\text{TaCl}_5 : \text{Ta}_2\text{O}_5$ , finding  $\text{Ta} = 181.45$ — $181.60$ ; mean  $181.52 \pm 0.02$ . Later, Sears and Balke (*ibid.*, 1915, 37, 833) concluded that determinations of the ratio  $2\text{TaCl}_5 : \text{Ta}_2\text{O}_5$  were untrustworthy owing to serious sources of error. They therefore attempted to find the ratio  $\text{TaCl}_5 : 5\text{Ag}$ , and from three series of determinations found  $\text{Ta} = 181.77$ ,  $181.31$ , and  $181.03$ , which gave on combination the general mean  $181.29 \pm 0.20$ . The poor agreement between the three series of results was later explained by Balke (*ibid.*, 1917, 39, 1852) as being due to uncertainty arising out of the analytical procedure employed, and he concluded that tantalum pentachloride was unsuitable for use in atomic-weight determinations (see p. 1289).

All the figures given above are on the basis of the recalculated data published by F. W. Clarke ("A Recalculation of the Atomic Weights," 1920), who summarised the situation thus: "So far as present evidence goes it seems probable that the atomic weight of tantalum is somewhere near 181 with an uncertainty of at least half a unit." This remark is equally applicable now, for no fresh

evidence has appeared. In 1912, the International Committee on Atomic Weights gave the value of tantalum as 181.5, which is still used by the German (*Ber.*, 1930, **63**, 1) and American (*J. Amer. Chem. Soc.*, 1929, **51**, 653) Chemical Societies, but in 1929 the Chemical Society (*J.*, 216) changed it to 181.3, the value deduced by Clarke (*op. cit.*) from the results of Sears and Balke (*loc. cit.*).

### *Purification of Materials.*

**Water.**—The distilled water of the laboratory was redistilled from a faintly alkaline, dilute permanganate solution and then redistilled in an all-silica still and condenser. The purified water was found by nephelometric test to be halogen-free and was collected and stored in stoppered Pyrex flasks.

**Nitric Acid.**—Merck's "pure" acid was redistilled in an all-silica still and condenser, and the middle fraction, which was found to be halogen-free, was collected and similarly stored.

**Oxalic Acid.**—"A.R." Material supplied by the British Drug Houses, Ltd., was used directly, since it dissolved completely in water and was also free from iron as well as halogens.

**Chlorine.**—The source of this gas was a cylinder of the liquid supplied by the Imperial Chemical Industries, Ltd., and stated to contain only a trace of bromine. The gas was passed through an all-glass apparatus in which it was first dried by sulphuric acid contained in four wash-bottles, then freed from possible traces of hydrogen chloride by passage through two tubes containing ignited lime, as recommended by Hönigschmid (*Z. anorg. Chem.*, 1927, **163**, 315), and finally dried by passage through two tubes containing phosphoric oxide.

**Bromine.**—This had been prepared free from chlorine and iodine by Willard and McAlpine's method (*J. Amer. Chem. Soc.*, 1921, **43**, 799) and was from a stock prepared for an earlier work. Removal of traces of hydrobromic acid was effected by keeping it over calcium oxide as recommended by Hönigschmid and Zintl (*Annalen*, 1923, **433**, 217).

**Argon.**—The gas from a steel cylinder of compressed argon was purified in an all-glass apparatus by bubbling through sulphuric acid and passing successively over soda-lime, hot copper and copper oxide, hot magnesium ribbon, and finally again over hot copper oxide and copper; it was then stored in galvanised-iron holders. As it was not considered necessary for this work to free it completely from nitrogen, it was passed through the purification train only once.

**Sodium Chloride.**—Kahlbaum's "pure" salt was reprecipitated twice from a filtered aqueous solution by passage of hydrogen



chloride, and the product was recrystallised from water and fused in a platinum basin.

*Potassium Bromide.*—Kahlbaum's "pure" salt was recrystallised twice from water, the crystals being drained centrifugally and fused in platinum.

*Silver.*—This was obtained from a stock prepared for an earlier work by following the method of Richards and Wells (*J. Amer. Chem. Soc.*, 1905, 27, 472), and fused on a magnesia support in a vacuum.

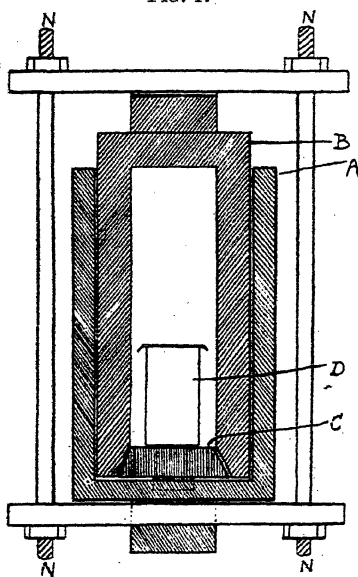
*Preparation of Tantalum.*—Although tantalum of a high degree of purity is commercially available, no details are to be found in the literature regarding the conditions governing its preparation in a pure state. Von Bolton (*Z. Elektrochem.*, 1905, 11, 45), who achieved a purity of 99%, merely mentions that he used a "modification" of the process by which Berzelius (*Pogg. Annalen*, 1825, 4, 10) and Rose (*ibid.*, 1856, 99, 60) had been unable to obtain metal of more than 58% purity; he effected further purification by fusing the compressed powdery material in a vacuum arc furnace. Spitzin and Kaschtanoff (*Z. anorg. Chem.*, 1929, 182, 207) state that their attempts by an improved Berzelius-Rose method yielded metal of only 95% purity. Since it appears that very pure tantalum cannot be prepared by other methods of reduction (e.g., Moissan, *Compt. rend.*, 1902, 134, 211; Goldschmidt, *Z. angew. Chem.*, 1898, 11, 823; Ruff and Thomas, *Z. anorg. Chem.*, 1925, 148, 18; Muthmann, Weiss, and others, *Annalen*, 1904, 337, 387; 1907, 355, 62), and as it was not considered feasible to study electrolytic methods (e.g., Bouhard, French Patent, 1907, 377931; Weintraub, U.S.P. 1910, 947983), it was decided to investigate the Berzelius-Rose method under improved conditions which included those indicated by Balke (*Chem. Met. Eng.*, 1922, 27, 1272; 28, 560). Briefly, it consisted in the preparation of the metal by the fusion of potassium tantalifluoride with sodium under conditions which minimised the formation of oxides of tantalum and sodium tantalate.

The starting material was the double fluoride obtained from Merck as well as Kahlbaum. Both the specimens contained nearly 1% of silica and small traces of iron, manganese, titanium, and niobium. Removal of silica was effected by treatment with sulphuric acid as described by Balke (*J. Amer. Chem. Soc.*, 1905, 27, 1142). The silica-free preparation was purified according to Meimberg and Winzer's method (*Z. angew. Chem.*, 1913, 26, 157), and finally recrystallised by cooling from its saturated solution at 100° in 5% hydrofluoric acid, all the crystallisations being done in platinum basins. The crystals were transferred to a stout gutta-percha suction funnel and freed as far as possible from mother-

liquor, after which they were centrifuged in a cylinder of platinum gauze. They were dried over caustic potash in a vacuum desiccator and preserved in small cardboard boxes lined with filter paper.

*The reduction process.* This had to be carried out in the absence of air and moisture; otherwise, oxides of tantalum and sodium tantalate would be formed in considerable quantities, and the removal of even small traces of oxide from the metal can be accomplished only by heating at a very high temperature—probably above  $1500^{\circ}$ —in a high vacuum. The bomb employed for the process is shown diagrammatically in Fig. 1. It consisted of a thick

FIG. 1.



steel cylinder (A) open at the top and having a recess at the bottom to take the solid steel piece (C), the top of which was turned to fit accurately a conical taper in the hollow steel vessel (B). A trace of oil on the taper was enough to secure good fitting when the bolts (N, N) were tightened. The clearance between A and B was about 1 mm., so that they could be welded together in case the tapering joint proved unsatisfactory. The reaction vessel D, made from a sheet of the purest commercial molybdenum, seemed to resist attack during the reaction.

The actual manipulation during an experiment was as follows. The shell A containing the block C and the reaction vessel D was

dried by being heated whilst a stream of argon passed through it. Pure freshly dried potassium tantalifluoride (50 g.) and Merck's sodium (18 g.), freshly cut into small pieces under dry benzene, were alternately transferred in small quantities to the reaction vessel while a stream of argon was circulating in the shell. The reaction vessel was then covered with its lid, the vessel B kept in position, and the bolts tightened. The bomb was now heated by burners and kept at a dull red heat for about an hour; its lower portion was then cooled quickly by a jet of water while two tubes were delivering argon near its top. After cooling to room temperature, the bomb was opened and the contents of the reaction vessel, which still contained some free sodium, were transferred in small quantities to

water (300 c.c.) contained in a large platinum basin, whereupon most of it disintegrated to a black powder, the few lumps remaining being crushed with a clean steel rod.

*Purification of the crude metal.* The powdery material in the dish was washed five or six times by decantation with cold water and then several times with dilute alcohol (25%), as recommended by Rose (*loc. cit.*), until the removal of soluble salts was practically complete. It was then digested with three successive portions of hot nitric acid (*d* 1.20), well washed with water, digested twice with hot hydrochloric acid (1 : 1), again washed with water, and finally dried in a stream of argon at about 300°. The dried powdery material was found to contain 97.9% of free tantalum. The powder was compressed into pellets, each weighing nearly 5 g., in a nickel-steel die at pressures ranging from 20,000 to 30,000 lb. per sq. in. and the pellets were freed from gas by 10 hours' heating at about 1000° in a vacuum of  $10^{-4}$ — $10^{-5}$  mm. They were then heated inductively in a vacuum furnace in a crucible of pure thoria, a current of 180 amps. at 7000 volts and 490,000 cycles being used. The vacuum maintained was about  $10^{-5}$  mm., and temperatures of 1700—1800° were reached. After this treatment the pellets were found to have sintered to a hard mass with a platinum-grey lustre, and oxidation experiments showed them to contain 99.2% of free tantalum. The remaining 0.8% was deemed to be tantalum oxide, since a spectrographic study of the metal did not reveal the presence of foreign metals.

#### *The Method of the Determinations.*

The method consisted in the preparation of the chloride and the bromide of tantalum by direct union, their purification by distillation and sublimation in a vacuum, and collection in sampling bulbs which were evacuated and then sealed for analysis. The bulb containing the halide was weighed and then broken under a dilute solution of ammonia whereby all the halogen was converted into the ammonium halide, which could be transferred to another vessel for halogen estimation. The insoluble tantalic acid, formed by the hydrolysis of the sample, and the glass fragments resulting from the breaking of the bulb were then digested with a hot solution of oxalic acid, whereupon all the tantalic acid went into solution. The glass pieces that remained were weighed in order to obtain the weight of the sample originally in the bulb. The estimation of halogen was carried out both nephelometrically and gravimetrically by the method of Richards as adopted by Hönigschmid. The ratios  $\text{TaBr}_5 : 5\text{Ag} : 5\text{AgBr}$  and  $\text{TaCl}_5 : 5\text{Ag} : 5\text{AgCl}$  so obtained enabled the calculation of the atomic weight of tantalum on the

assumption that the values for silver, bromine, and chlorine were 107.880, 79.915, and 35.457 respectively.

The analytical part of this work, including weighings, was carried out in special rooms which were free from acid fumes and were illuminated only by ruby light.

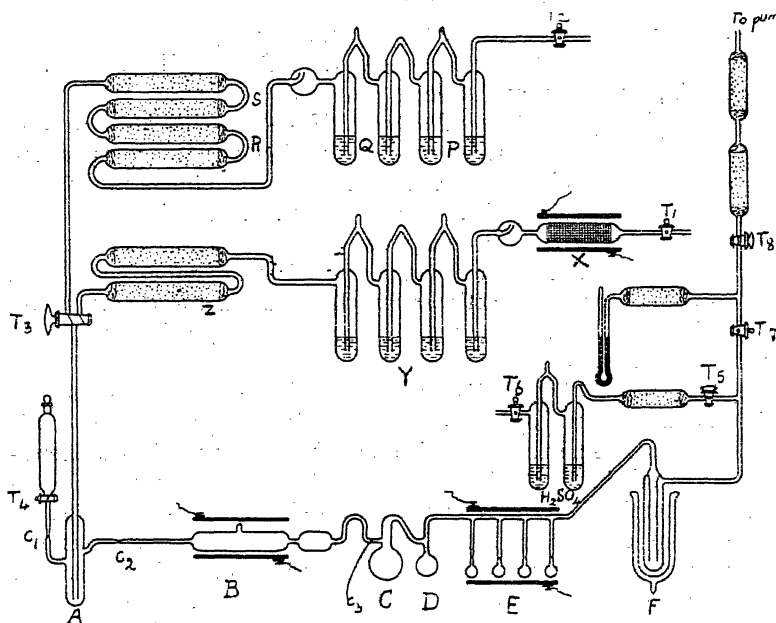
*Balance and Weighing.*—The weights were standardised by the method of Richards (*J. Amer. Chem. Soc.*, 1900, 22, 144), and the weighings performed in a room which was maintained by electrical heaters at a constant temperature of  $20^{\circ} \pm 0.1^{\circ}$ . The balance employed was of the special type made by Oertling with a beam of invar-steel which was protected by an aluminium partition and provided with a prism and mirror device to enable movements of the beam to be noted with a lamp and scale fixed at a distance of 2 m. from it. The weighings were done by the method of counterpoise and substitution, and the weights so obtained were corrected for errors due to inequality of weights and reduced to vacuum. Successive weighings of the same object usually agreed to 0.01 mg. and never differed by more than 0.02 mg.

*The Distillation Apparatus.*—This resembled the apparatus devised by Willard and McAlpine (*loc. cit.*) and is shown diagrammatically in Fig. 2. It consisted of a bubbler (*A*) into which bromine could be introduced through a side tube and separating funnel, a tube (*B*) in which powdered tantalum could be kept heated, the distillation bulbs (*C* and *D*), and the system of sampling bulbs (*E*). The three-way tap  $T_3$  served to introduce either argon or chlorine into the apparatus. Argon entered from a gas-holder through the tap  $T_1$ , and passed over copper gauze kept at  $500\text{--}550^{\circ}$  in *X*, through sulphuric acid in *Y*, and phosphoric oxide in *Z*; whereas chlorine entered through the tap  $T_2$  and, after bubbling through a strong solution of potassium permanganate in *P* and sulphuric acid in *Q*, passed over ignited lime in *R* and phosphoric oxide in *S*. A continuous flow of either gas through the apparatus could be maintained by keeping open  $T_1$  or  $T_2$  and also  $T_3$ ,  $T_5$ , and  $T_6$  while the other taps were kept closed. With taps  $T_7$  and  $T_8$  open and all the others closed, the apparatus could be evacuated by a mercury-vapour pump working in conjunction with a "Hyvac" pump. The trap *F*, which was cooled in liquid air, served not only to freeze bromine or chlorine, which would otherwise pass into the pumps, but also to minimise diffusion of mercury vapour into the apparatus. All the taps in the apparatus were lubricated with metaphosphoric acid.

*The Preparation of Tantalum Bromide.*—The parts *A* to *E* of the apparatus were kept at  $300\text{--}350^{\circ}$  and thoroughly dried and freed from air by alternate evacuation and filling with argon, the process

being repeated 5 or 6 times. Then, with a stream of argon flowing through the apparatus, the tip of the side tube attached to *B* was broken to introduce 7–8 g. of finely powdered tantalum, which had been previously dried in a current of argon. The tube was now sealed off and the apparatus evacuated and refilled with argon, thus ensuring the total absence of air and moisture from the system. Through some phosphoric oxide, which was kept in the separating funnel, somewhat more than twice the quantity of bromine necessary to react with the tantalum taken was run into the bubbler *A*, entry of air being prevented by closing the tap of the funnel while

FIG. 2.



there was still about 1 c.c. of bromine in it. The constriction  $c_1$  was then sealed. The furnace surrounding the tube *B* being kept at 650–700°, a beaker of water at about 55° was placed under the bubbler, and a slow stream of argon bubbled through, carrying bromine vapour to the hot tantalum in *B*. The initial formation of the bromide was immediate, although it continued slowly, much bromine escaping combination. By suitably warming the tube connecting *B* and *C*, and keeping *C* and *D* cool, most of the bromide was collected in *C*; some of it, however, went into *D*, and a small quantity was carried still farther in a thin cloud by the gas stream. At the same time, some drops of bromine collected in *C* and *D* and

also in some parts of the system *E*. When enough of the bromide had been prepared, the argon supply was stopped and the preparation tube *B* allowed to cool. The apparatus was then sealed at the constriction  $c_2$ , heated at 100–110°, and evacuated so as to remove all free bromine. The constriction  $c_3$  was now sealed and the tube *B* removed. With the pump in continuous operation, the bulb *C* was kept at about 300° in order to drive most of the bromide into the bulb *D*, which was kept cool. The constriction (not shown in the diagram) in the tube connecting *C* and *D* was then sealed. The sublimation of the bromide from *D* into the bulbs *E* was effected by suitable movement of the furnace, which was maintained at about 300°. With the vacuum pump in continuous operation the bulbs were finally sealed for analysis.

The bromide in the bulbs consisted of fine needles as well as some thin, lemon-yellow leaflets.

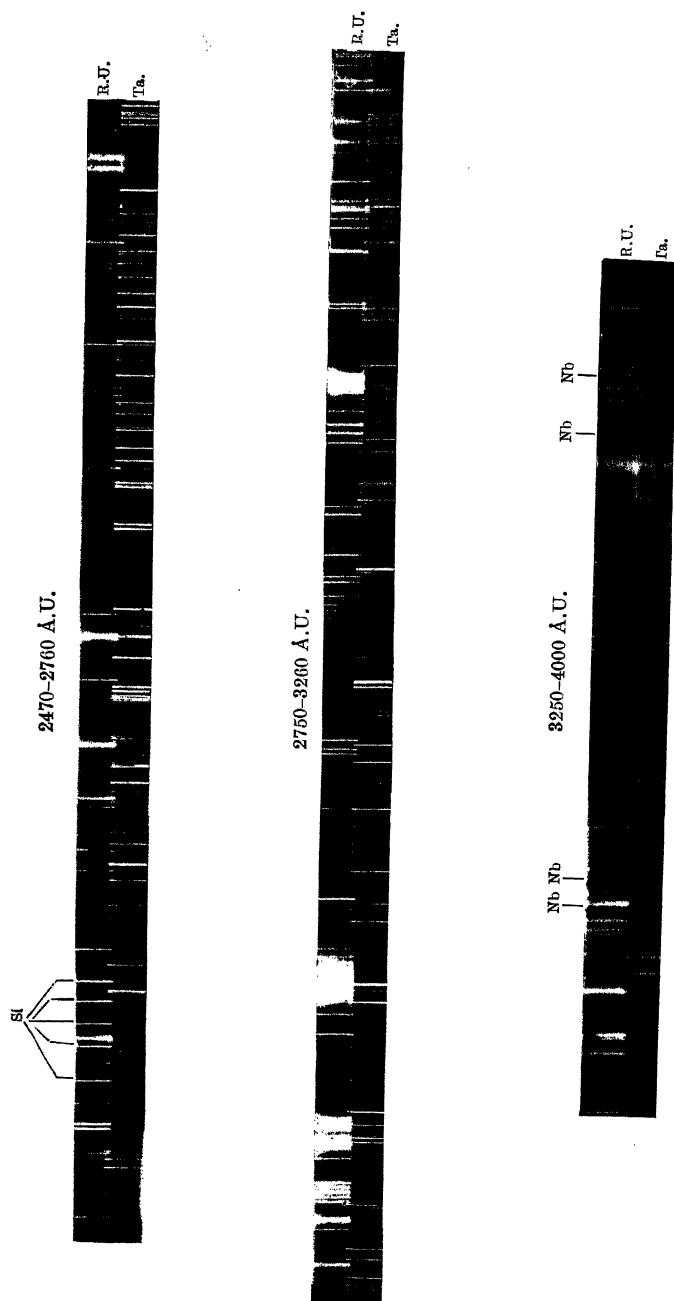
*Preparation of Tantalum Pentachloride.*—The chloride was prepared in an apparatus which was exactly like the foregoing except that it had no bubbler, the tube *B* being directly joined to the three-way tap by a tube having a constriction. The subsequent procedure was similar to that employed for the bromide, a slow stream of dry chlorine being passed over the powdered metal at 550–600°.

The chloride was perfectly snow-white during the earlier stages of the distillation, but later acquired a pale creamy colour, probably owing to prolonged heating.

*Spectrographic Studies of the Purity of the Tantalum Preparations.*—The instrument employed was a quartz Littrow spectrograph made by A. Hilger. The principle of the method consisted in the identification of the impurity lines in the spectrum of the tantalum compounds examined, by measurement as well as by superposition on the spectra of the probable impurities. The first step was the preparation of photographs of the ultra-violet and visible arc spectra of the tantalum compounds between copper poles, and also corresponding photographs of the copper arc. A series of photographs was prepared of the spectra of silica, iron, manganese, niobium, titanium, and molybdenum in the copper arc, each on a separate plate. The persistent lines of these elements were identified by measurement and suitably marked on the plates. By bringing each of these impurity spectra into juxtaposition with the tantalum spectrum, it was easy to note if any of the impurity lines were present in the latter, but as none of these could be traced it was decided to make an exhaustive examination for all the possible impurities by the R.U. (raies ultimes) powder method advocated by A. Hilger. Since the R.U. powder contains only small traces of nearly all the metals in a suitable diluent, its arc spectrum, although



Fig. 3.





consisting of only a limited number of lines, includes all the strongest lines of all the elements in it. Therefore, by photographing the R.U. spectrum in juxtaposition with that of the specimen to be examined, it is a relatively simple matter to ascertain the impurities present; moreover, it is possible, within certain limits, to estimate quantitatively the impurities according to the order of sensitivity of the lines observed. An examination of the spectrum photographs (Fig. 3) will make this matter clear. Niobium, for instance, is present in the R.U. powder to the extent of about 0.05%, but it gives about 15 lines, some of which are marked on the plate. Since not even one of these can be traced in the tantalum spectrum, it is concluded that niobium is absent. Similarly with most of the other elements. The results, however, are not so definite in the case of silica. It will be seen from the plate that the group of lines marked Si (2506.9—2528.5 Å.U.), which are strong in the R.U., are present in the tantalum spectrum also, though with a smaller intensity. Since, however, this group of lines is present in the spectrum of the poles themselves and with an intensity approximately equal to that in the tantalum spectrum, it can be deduced that the tantalum is practically free from silica. The other metals regarding which there is similar uncertainty are calcium and magnesium. The quantity in which they are present must, however, be very small. Dr. J. W. Ryde and Mr. H. G. Jenkins, of the Research Laboratories of the General Electric Co., Ltd., who developed the R.U. method, kindly undertook a confirmatory examination of these specimens and reported that spectroscopically they were unable to find impurities. There is, however, the possibility that silica, calcium, and magnesium may be present to a total extent of about 0.05%.

*Determination of the Ratios TaBr<sub>5</sub> : 5Ag : 5AgBr.*—The bulb containing the bromide was cleaned and dried as usual (compare Baxter, *Proc. Amer. Acad. Arts Sci.*, 1924—25, 60, 228), and its weight in air determined. It was then weighed in water by suspending it with a thin platinum wire, and from the observed loss of weight the vacuum correction was calculated in the usual manner. It was then placed on the bottom of a thick-walled conical Pyrex flask containing about 400 c.c. of a ca. 3% solution of ammonia, and broken by a blunt glass rod, which was quickly rinsed and removed. The flask was immediately stoppered, left for about 2 hours, and then rotated so as to disturb the flocculent precipitate which had settled, this operation being repeated 4 or 5 times at intervals of about an hour. After standing over-night, the clear supernatant liquid was poured through a Jena-glass Gooch crucible having a sintered-glass filter, and the filtrate caught directly in a large conical precipitation flask, made of Pyrex glass and kept inside an evacuated

bell-jar. The material remaining in the original flask, viz., the precipitate of tantalic acid and the glass fragments of the bulb, was washed by decantation 10—12 times with 70—80 c.c. portions of a hot (60°) 1% aqueous solution of ammonium nitrate, as recommended by Biltz and Voigt (*Z. anorg. Chem.*, 1922, **120**, 171), with the modification that it contained nearly 2% of free nitric acid in addition. The clear wash-liquids were passed through the Gooch crucible in each case, and the filtrates added to the first filtrate, which thus increased to about 1200 c.c. and was preserved for halogen estimation. The washing process was effective because the tantalic acid settled easily in the wash-liquid and so facilitated the decantation. It is shown later (p. 1291) that the washed residue was halogen-free and that practically none of it (either tantalic acid or glass) was transferred from the flask during washing.

To dissolve out the tantalic acid in order that the glass pieces might be weighed, the residue in the flask was digested on a boiling water-bath for about 2 hours with some 50 c.c. of a saturated solution of oxalic acid. The liquid in the flask was then diluted with about 300 c.c. of water, whereupon the solution became quite clear and was free from any particles of tantalic acid. The glass fragments appeared quite clean and transparent. The clear liquid was poured through a weighed silica Gooch crucible with a sintered-silica filter. The glass pieces were washed by decantation 10—12 times with 50 c.c. portions of warm water, then transferred with a jet of water to the crucible, dried, and weighed. (The washings from the above operations were discarded.) The glass pieces were dried slowly by being kept at 90—110° for about 2 hours and then at 400—420° for about 8 hours; and their weight was corrected to vacuum and subtracted from the corrected weight of the bromide bulb in order to obtain the weight of the bromide originally in the bulb. This was, however, corrected for a small error (0.03 mg.) which appeared to be incidental to the collection and weighing of the glass fragments (see p. 1291).

The estimation of halogen in the bromide solution, which contained only nitric acid and ammonium bromide and nitrate, was carried out according to the Harvard methods as developed by Hönigschmid. The standard solutions of silver nitrate and potassium bromide required to make up for the deficiency of either silver or bromide ions in the analytical solution, and for the generation of opalescence in the test mixtures, were all made up with the concentrations recommended by the author mentioned above. On the assumption that  $Ta = 181.37$ , which was calculated from the mean of two gravimetric determinations of the ratio  $TaBr_5 : 5AgBr$ , a quantity of silver was weighed out which was insufficient by about

0.1—0.2 mg. to precipitate quantitatively the bromide ion in the analytical solution. The silver was dissolved in about 50 c.c. of nitric acid ( $d$  1.20) in a conical Pyrex flask having a four-bulbed tube ground into its neck. After being gently boiled for a few minutes, the solution was diluted to about 0.1*N* and then transferred quantitatively to the flask containing the bromide solution, which was then stoppered, and shaken at frequent intervals. After standing for about 48 hours, the precipitate was found to have settled completely, leaving the supernatant liquid perfectly clear. Two 25-c.c. portions of the clear liquid were withdrawn and tested for excess of bromide or silver by addition of 1 c.c. of silver solution (1 in 1000) to one and 1 c.c. of an equivalent bromide solution to the other. The test solutions were allowed to stand for 4 hours with frequent stirring with glass rods, and then examined in a nephelometer of the Kober type with a Klett top-reader. According as the tests indicated excess of bromide or silver, standard solution of silver (0.1 in 1000) or equivalent bromide solution was added to the analytical solution until a nephelometric test indicated that the two ions were in exact equivalence as revealed by the equality of the intensity of opalescence developed when equal portions of the solution were treated with equivalent quantities of either silver or bromide test solution. After the end-point had been reached, excess of one of the standard solutions was added, and the end-point again obtained by back-titration in the nephelometer. The quantity of silver (in the standard solution) introduced in order to reach the point of equivalence was added to the weight of silver originally added in bulk to the analytical solution, and the ratio  $\text{TaBr}_5 : 5\text{Ag}$  calculated. The results of the determinations are given in Table I (a).

After completion of the nephelometric titration, 25 c.c. of *N*/10-silver nitrate solution were added to the contents of the flask in order to precipitate all the dissolved silver bromide. The flask was stoppered and occasionally shaken during the next 24 hours, and the precipitate then allowed to settle. The clear liquid was poured through a weighed Jena-glass Gooch crucible with a sintered-glass filter. The silver bromide in the flask was washed ten times by decantation with about 60 c.c. portions of 0.5% nitric acid, transferred to the crucible, dried for about 18 hours at 300—320°, and weighed. Most of the silver bromide was transferred to a porcelain crucible and fused in an electric furnace maintained at 500—520°; it was then seen to be transparent and free from dark patches—a clear indication of its purity. In two experiments in which the silver bromide was weighed both before and after fusion, the loss (due to expulsion of the last traces of moisture) was not more

than 0.02 mg. Since this result is in agreement with the long experience of Hönigschmid that silver bromide dried at  $300^{\circ}$  does not retain an appreciable amount of moisture, no attempts were made to determine the loss on fusion in every experiment. Confirmatory evidence regarding the purity of the silver bromide precipitate was obtained from determinations of the ratio  $\text{AgBr} : \text{AgCl}$  (see p. 1292).

The weight of the silver bromide obtained by weighing the dried precipitate was corrected for the quantity which escaped weighing owing to solution in the nitric acid washings, and also for the small amount which was retained by the walls of the precipitation flask. The estimation of these two sources of error was carried out jointly as recommended by Hönigschmid (*Z. anorg. Chem.*, 1924, **136**, 278; *Annalen*, 1923, **433**, 201), i.e., by dissolving out the traces of the silver bromide in the precipitation flask by the addition of ammonia, adding this solution to the nitric acid washings\* of the silver bromide, diluting the combined solution to a known volume, and comparing it nephelometrically with solutions containing known amounts of silver bromide. The quantity of silver bromide so estimated was added to the weight of the precipitate, and the ratio  $\text{TaBr}_5 : 5\text{AgBr}$  calculated. Table I (b) gives the results of the determinations.

*Determination of the Ratios  $\text{TaCl}_5 : 5\text{Ag} : 5\text{AgCl}$ .*—The sealed bulbs containing the chloride were weighed in air and in water, and then broken under a solution of ammonia. The subsequent procedure was exactly as in the case of the bromide, except that sodium chloride was substituted for potassium bromide in the solutions employed during the nephelometric determinations. The silver chloride precipitate was dried at  $300\text{--}320^{\circ}$  for about 18 hours before weighing. It always fused to a transparent, light amber-coloured mass, free from any dark patches: this was considered to be a definite indication of its purity. The results of the various determinations are given in Table II, all the weights being reduced to vacuum. The atomic weights of silver, bromine, and chlorine were assumed to be as on p. 1282.

The individual values for the atomic weight given in Table I(a) show an extreme variation of 0.03 unit (1.7 parts per 10,000). Their mean variation is 0.008 unit (0.5 part per 10,000) from the mean value 181.36, the probable error of which is found to be  $\pm 0.003$  unit.

\* These washings were collected separately from the mother-liquor from which the precipitation was made. The mother-liquor was discarded, as the quantity of silver bromide in it must have been negligible owing to the excess of silver nitrate present.

TABLE I.

No.	TaBr <sub>5</sub> , g.	(a) Ratio TaBr <sub>5</sub> :5Ag.			(b) Ratio TaBr <sub>5</sub> :5AgCl.		
		Ag, g.	TaBr <sub>5</sub> :5Ag.	Ta =	AgBr, g.	TaBr <sub>5</sub> :5AgBr.	Ta =
1	3.07127	—	—	—	4.96415	0.61869	181.36
2	3.72095	—	—	—	6.01413	0.61870	181.37
3	3.81890	3.54594	1.07698	181.34	6.17267	0.61868	181.35
4	3.59654	3.33939	1.07700	181.36	5.81303	0.61870	181.37
5	2.69071	2.49831	1.07701	181.37	4.34926	0.61866	181.33
6	2.61163	2.42488	1.07702	181.37	4.22133	0.61868	181.35
7	3.92094	3.64064	1.07699	181.35	6.33750	0.61869	181.36
8	2.04583	1.89956	1.07700	181.36	3.30681	0.61867	181.34
(a) Total	18.68455	17.34872	1.07700	181.36	—	—	—
(b) „	25.47677	—	—	—	41.17888	0.61868	181.35

The corresponding variations in Table I (b) are 0.04 and 0.011 unit respectively, giving a mean of 181.35 with a probable error of 0.004.

TABLE II.

No.	TaCl <sub>5</sub> , g.	(a) Ratio TaCl <sub>5</sub> :5Ag.			(b) Ratio TaCl <sub>5</sub> :5AgCl.		
		Ag, g.	TaCl <sub>5</sub> :5Ag.	Ta =	AgCl, g.	TaCl <sub>5</sub> :5AgCl.	Ta =
1	3.15350	4.74301	0.66488	181.35	6.30152	0.50044	181.37
2	2.96215	4.45549	0.66483	181.33	5.91874	0.50047	181.40
3	4.08061	6.13756	0.66486	181.34	8.15438	0.50042	181.36
4	3.21073	4.82972	0.66479	181.30	6.41613	0.50042	181.36
5	3.49922	5.26278	0.66490	181.36	6.99201	0.50046	181.39
Total	16.90621	25.42856	0.66485	181.34	33.78278	0.50044	181.37

The individual values for the atomic weight given in Table II(a) show an extreme variation of 0.06 unit (3.3 parts per 10,000). Their mean variation is 0.019 unit (1.0 part per 10,000) from the mean value 181.34, the probable error of which is found to be  $\pm 0.007$  unit.

The corresponding data for Table II (b) are 0.04 and 0.015 unit, the mean atomic weight being  $181.37 \pm 0.004$ .

*Summary of Results.*—The mean values obtained from the four series of determinations are collected in the following table, from which it will be seen that the most probable value for the atomic weight of tantalum is 181.36.

Ratio.	No. of expts.	Mean value for at. wt. of Ta.	Probable error.
TaBr <sub>5</sub> :5Ag .....	6	181.36	$\pm 0.003$
TaBr <sub>5</sub> :5AgBr .....	8	181.35	0.004
TaCl <sub>5</sub> :5Ag .....	5	181.34	0.007
TaCl <sub>5</sub> :5AgCl .....	5	181.37	0.004
General mean		181.357	0.0002

#### *Investigation of Some Possible Sources of Error.*

Sears (*loc. cit.*) found that, although tantalum pentachloride exists as a stable compound in an atmosphere of dry nitrogen and does not occlude chlorine, it is unsuitable for use in work where a high

degree of accuracy in its analysis is desired. This conclusion was based on the following observations: (a) Broken glass cannot be filtered off from the hydrolysed tantalum chloride because of the insoluble tantalic acid formed; (b) tantalum pentachloride cannot be weighed accurately in a vessel with a ground joint owing to hydrolysis caused by moist air diffusing in through the joint; (c) volatility of glass during fusion prevents an accurate estimate of the weight of tantalum pentachloride contained in a sealed glass tube of known weight; (d) when tantalum chloride is sealed in a glass bulb, some of it gets melted into the glass at the point of sealing.

The present work seems to be free from any of the above-mentioned sources of complication. The first did not arise because the tantalic acid could be completely dissolved out and so permitted the determination of the weight of the glass pieces. The second and third sources of error were avoided in the method employed for determining the weight of the sample: volatility of glass during fusion is a negligible factor, for Briscoe and Little (J., 1914, 105, 1315) and Weatherill (*J. Amer. Chem. Soc.*, 1924, 46, 2437) experienced no difficulty from that source. The last objection seems to be due to the tantalum pentoxide formed by hydrolysis of the chloride owing to the presence of moisture in the system. The tantalum chloride and also the tantalum bromide bulbs prepared in the earlier experiments had the appearance of frosted glass close to the point of sealing. The bulbs prepared in the later experiments and used for analysis were, however, free from this defect.

As spectrographic investigation afforded definite evidence that the tantalum halides prepared for analysis were almost entirely free from foreign metals, and as contamination from oxygenated compounds was obviated by carrying out the preparation and weighing in the absence of oxygen, air, and moisture, little uncertainty could be entertained regarding their purity. The method of analysis, however, involved several steps which demanded scrutiny.

A study was made of the process employed for washing the tantalic acid and glass fragments in order to extract all the halide present. As in every experiment the clear liquid was filtered through a Gooch crucible, it was easy to test whether any solid material was conveyed to it, by weighing the crucible before and after the filtration. Three experiments were performed with two different crucibles and the observed variations in weight were  $+0.02$ ,  $0.00$ , and  $+0.03$  mg., respectively, giving an average increase in weight of  $0.02$  mg. If this increase is due solely to tantalic acid, it is of no significance, since the crucibles employed

for this process were never used for the collection of either glass fragments or silver bromide precipitate; if it is due entirely to fine particles of glass, this would be a source of error, for this amount of glass would escape weighing and the apparent weight of the tantalum halide would be too high to this extent. Since, however, 0.02 mg. is within the limit of error of the determinations, the precise cause is immaterial.

The next point tested was whether any portion of the glass fragments was lost owing to solution, either colloidal or otherwise, in the wash-liquid. Bulbs similar to those employed for collecting the tantalum halides were fused on to a vacuum line and then sealed after evacuation. They were weighed in air and in water so as to obtain their weight in vacuum. They were then broken under a solution of 3% ammonia contained in a conical Pyrex-glass flask, and subjected to exactly the same treatment as the glass fragments in the actual determinations, *viz.*, washing with ammonium nitrate, decantation of the clear liquid, digestion with hot saturated solution of oxalic acid, and washing with water. They were then collected in a weighed Gooch crucible, dried as usual, and weighed. This weight was reduced to vacuum and compared with the weight of the bulb as determined at the beginning of the experiments; the results were as follows:

Bulb, g. ....	1.81427	1.70330	1.74959	1.68884
Glass pieces, g. ....	1.81425	1.70325	1.74958	1.68880
Difference, mg. ....	0.02	0.05	0.01	0.04

They indicate a definite average loss of 0.03 mg. This quantity was therefore added to the weight of glass as actually determined.

The next point to be tested was whether the process of washing removed the bromide quantitatively and left the residue of tantalic acid and glass fragments bromide-free. Although aqueous extracts of the residue failed to give any test for halogen, it was feared that adsorption of bromide ions might have proceeded in such a way as to escape detection in this manner. The material was therefore heated with sulphuric acid and tested for formation of hydrogen bromide. This was done by introducing the tantalic acid (and glass pieces) into a bulb (50 c.c.) through a side tube with a ground joint to accommodate a separating funnel. The condensing tube, which was fused to the bulb, was bent at right angles. With the end of the condensing tube dipping in 25 c.c. of 0.1*N*-silver nitrate solution, 10–15 c.c. of sulphuric acid ( $d$  1.84) were introduced into the bulb through the separating funnel, the tap of which was afterwards closed. The bulb was then heated in a bath at 120–125°. The silver nitrate solution remained clear without developing any opalescence. The distilling bulb was then allowed to cool, 0.05 mg.

of ammonium bromide (0.5 c.c. of 0.1 in 1000 solution) introduced into it, and the bulb reheated. The silver nitrate solution became strongly opalescent in less than 5 minutes. As the above test is very delicate, and as three lots of washed tantalic acid did not respond to it, it was concluded that the extraction of the halide was quite satisfactory.

The purity of the silver bromide precipitate was indicated by its appearance on fusion as already stated, and was confirmed by its conversion into silver chloride as follows. A portion of the dried silver bromide was transferred to a weighed porcelain crucible and fused in an electric furnace. The weight of the fused silver bromide was ascertained by reweighing the crucible. The crucible was then suitably supported in the centre of the furnace, which was maintained at about  $500^{\circ}$  while a stream of chlorine passed through it. After 5–6 hours, the chlorine supply was replaced by argon for about 2 hours in order to expel all the free chlorine. The crucible was then taken out of the furnace, cooled, and weighed. The results of three such experiments were :

AgBr, g. ....	4.16021	6.30116	5.99453
AgCl, g. ....	3.17510	4.80924	4.57492
AgBr/AgCl .....	1.31026	1.31022	1.31030

The mean of the three determinations ( $\text{AgBr/AgCl} = 1.31026$ ) is in tolerable agreement with the value obtained by Baxter (*Proc. Amer. Acad. Arts Sci.*, 1905, **41**, 82; 1906, **42**, 201), viz., 1.31017, thereby showing that the silver bromide formed in these experiments was adequately pure.

#### *Summary.*

Pure tantalum, prepared by a modified Berzelius–Rose method, was employed for the preparation of its bromide and chloride by direct union with the elements in an inert atmosphere. The halides were purified by distillation and sublimation in a vacuum, and collected in sampling bulbs for analysis. Spectrographic examination gave satisfactory evidence regarding their purity. They were analysed both nephelometrically and gravimetrically by the Harvard method as developed by Hönigschmid. Twenty-four closely-agreeing results pointed to the value 181.36 for the atomic weight of tantalum.

In conclusion, I wish to express my gratitude to Professor F. G. Donnan, F.R.S., for having provided every facility and for kind encouragement throughout the course of this work. My best thanks are due to Messrs. S. Barratt, B.A., and J. M. Walter, B.Sc., for valuable suggestions relating to the spectroscopic methods



employed. My warmest thanks are also due to Dr. C. Sykes of the Research Laboratories of the Metropolitan Vickers Electrical Co., Ltd., Manchester, for assistance with the high-frequency furnace, and to Dr. J. W. Ryde and Mr. H. G. Jenkins of the Research Laboratories of the General Electric Co., Ltd., Wembley, for carrying out a confirmatory analysis of the tantalum specimens. My hearty thanks are due to Mr. Henry Terrey, M.Sc., for assistance in the preparation of this paper.

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#### CLXIV.—4-Sulpho-3-hydroxybenzoic Acid.

By MADHAVLAL SUKHLAL SHAH.

THE sulpho-*m*-hydroxybenzoic acid which is obtained by the sulphonation of *m*-hydroxybenzoic acid has now been prepared by a more convenient method than those described by Barth (*Annalen*, 1868, **148**, 38), Senhofer (*ibid.*, 1869, **152**, 102), and Remsen (*Z. Chem.*, 1871, 295): it consists in heating a mixture of *m*-hydroxybenzoic acid and sulphuric acid at 90° for 2 hours; the sulpho-*m*-hydroxybenzoic acid crystallises in large yield on cooling and there is no sign of any other product. The acid, when recrystallised from water, separates as  $C_7H_6O_6S \cdot 2\frac{1}{2}H_2O$ , m. p. 206°. Barth and Senhofer describe the acid, m. p. 208°, crystallising with  $1\frac{1}{2}$  molecules of water.

The author has confirmed Barth's observation (*loc. cit.*; *Annalen*, 1871, **159**, 230; contrast Remsen, *loc. cit.*) that no organic acid other than protocatechuic acid, m. p. 199°, is produced by fusion of the sulpho-*m*-hydroxybenzoic acid with alkali. Hence the sulphonic acid appears to be 4-sulpho-3-hydroxybenzoic acid.

In order to obtain further evidence the author studied the methyl ether of this acid, comparing it with the oxidation products of isomeric 3-methoxytoluenesulphonic acids described by Haworth and Lapworth (*J.*, 1923, **123**, 2982; 1924, **125**, 1299). The sulphonic acid methyl ether (I) crystallised as  $C_8H_8O_6S \cdot 2H_2O$  and gave characteristic *barium* and *potassium hydrogen* salts. The latter on trituration with phosphorus pentachloride produced a chlorosulphonyl-3-methoxybenzoyl chloride, m. p. 87°, which gave on treatment (a) with water, a chlorosulphonyl-3-methoxybenzoic acid, m. p. 214°, and (b) with ammonia, a sulphonamido-3-methoxybenzamide, m. p. 255°. The former when digested with ammonia

and the latter when hydrolysed with hydrochloric acid yielded the same sulphonamido-3-methoxybenzoic acid (II), m. p. 290° (decomp.).

Haworth and Lapworth (*loc. cit.*) state that their potassium hydrogen 4-sulpho-3-methoxybenzoate obtained from 3-methoxytoluene-4-sulphonic acid yielded 4-sulphonamido-3-methoxybenzoic acid, m. p. 255°, by the action of ammonia on the sulphonyl chloride, which was not isolated. From the author's results the substance, m. p. 255°, which Haworth and Lapworth describe under the name of sulphonamido-3-methoxybenzoic acid appears to be 4-sulphonamido-3-methoxybenzamide, m. p. 255°. In order to clear up this matter the experimental work of Haworth and Lapworth was repeated.

3-Methoxytoluene-4-sulphinic acid (III), prepared from 4-nitro-*m*-cresol via 4-nitro- and 4-amino-3-methoxytoluenes, was oxidised and 3-methoxytoluene-4-sulphonic acid and 4-sulpho-3-methoxybenzoic acid (I) were obtained. The latter gave, on treatment similar to that described above, 4-chlorosulphonyl-3-methoxybenzoyl chloride, m. p. 87°, 4-chlorosulphonyl-3-methoxybenzoic acid, m. p. 214°, 4-sulphonamido-3-methoxybenzamide, m. p. 255°, and 4-sulphonamido-3-methoxybenzoic acid (II), m. p. 290° (decomp.), identical with those obtained from the author's sulpho-*m*-hydroxybenzoic acid methyl ether, the conclusions being confirmed in each case by the mixed melting point test.

Haworth and Lapworth also state that their sulphonamido-3-methoxybenzoic acid, m. p. 255°, was produced when 3-methoxytoluene-4-sulphonamide (IV) was oxidised with alkaline permanganate. The author, however, obtained only 4-sulphonamido-3-methoxybenzoic acid, m. p. 290° (decomp.).

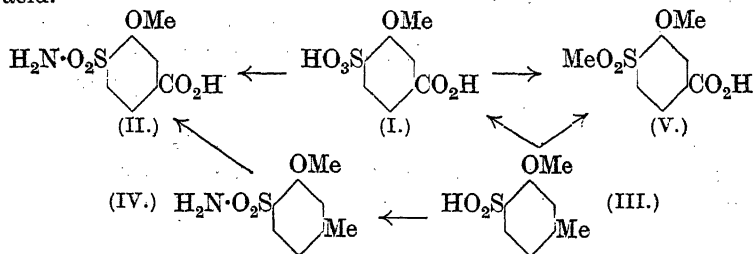
For full information the author converted (A) 4-sulpho-3-methoxybenzoic acid (I) and (B) 3-methoxytoluene-4-sulphinic acid (III), which yields 4-sulpho-3-methoxybenzoic acid as shown above, into 3-methoxybenzoic acid 4-methylsulphone (V).

(A) 4-Chlorosulphonyl-3-methoxybenzoic acid, m. p. 214°, prepared from sulpho-*m*-hydroxybenzoic acid methyl ether (I), was reduced by Gattermann's method (*Ber.*, 1899, **32**, 1136) and the 4-thiol-3-methoxybenzoic acid (monothiovanillic acid), m. p. 180°, which was obtained was converted on methylation into 4-methylthiol-3-methoxybenzoic acid (monothioveratric acid), m. p. 193°. The latter on oxidation gave 3-methoxybenzoic acid 4-methylsulphone (V), m. p. 227°.

(B) When 3-methoxytoluene-4-sulphinic acid (III) was similarly reduced, 4-thiol-3-methoxytoluene, b. p. 254°, was produced. This passed on methylation into 4-methylthiol-3-methoxytoluene, b. p. 269—270°. When the latter was oxidised with alkaline perman-

ganate, the same 3-methoxybenzoic acid 4-methylsulphone (V), m. p. 227°, as described in (A) was produced : a mixture of the two showed no depression in melting point. This proves that sulpho-*m*-methoxybenzoic acid (I) corresponds to 3-methoxytoluene-4-sulphinic acid (III) and that the sulpho-*m*-hydroxybenzoic acid is 4-sulpho-3-hydroxybenzoic acid.

The sulpho-*m*-hydroxybenzoic acid methyl ether (I) was also fused with sodium hydroxide and with potassium hydroxide with a view to get vanillic acid, but the product was protocatechuic acid. Partial fusion at a low temperature gave sulpho-*m*-hydroxybenzoic acid together with protocatechuic acid, which indicates that in alkali fusion 4-sulpho-3-methoxybenzoic acid (I) is first demethylated and then converted into 3:4-dihydroxybenzoic acid, *i.e.*, protocatechuic acid. Vanillic, *isovanillic*, and *veratric* acids have been found to be similarly demethylated and to yield protocatechuic acid.



#### EXPERIMENTAL.

*Sulpho-m-hydroxybenzoic Acid.*—*m*-Hydroxybenzoic acid (40 g.) was mixed with sulphuric acid containing 3% of sulphur trioxide (60 c.c.) and heated at 90° for 2 hours. The brown solution obtained solidified on cooling to a hard crystalline mass; this was crushed, washed with dilute sulphuric acid, and pressed and dried on porous tile. The crude substance crystallised from water (charcoal) in greenish-yellow needles or truncated prisms containing  $2\frac{1}{2}\text{H}_2\text{O}$ , m. p. 206° (yield, 61 g.). The substance effloresced on exposure to air and developed an intense violet fluorescence in dilute alkaline solutions (Found: equiv., 264, 263. Calc. for  $\text{C}_7\text{H}_6\text{O}_6\text{S}, 2\frac{1}{2}\text{H}_2\text{O}$ : equiv., 263). Desiccation removed  $1\frac{1}{2}$  molecules of water and left an opaque white mass, m. p. 213° (Found: equiv., 235.6. Calc. for  $\text{C}_7\text{H}_6\text{O}_6\text{S}, \text{H}_2\text{O}$ : equiv., 236).

The acid sodium, potassium and ammonium salts were prepared (1) by neutralising one half of an aqueous solution of sulpho-*m*-hydroxybenzoic acid with alkali and then mixing it with the other half, (2) by acidifying the neutral solution with hydrochloric acid.

The sodium hydrogen salt separated in shining plates and was recryst-

tallised for analysis (Found : Na, 8.6;  $\text{H}_2\text{O}$ , 10.1; equiv., 267.1.  $\text{C}_7\text{H}_5\text{O}_6\text{SNa} \cdot 1\frac{1}{2}\text{H}_2\text{O}$  requires Na, 8.6;  $\text{H}_2\text{O}$ , 10.1%; equiv., 267). The *potassium hydrogen* salt crystallised in prismatic plates and is more soluble than the acid sodium salt (Found : K, 14.1;  $\text{H}_2\text{O}$ , 6.51; equiv., 274.3.  $\text{C}_7\text{H}_5\text{O}_6\text{SK} \cdot \text{H}_2\text{O}$  requires K, 14.2;  $\text{H}_2\text{O}$ , 6.6%; equiv., 274.1). The *ammonium hydrogen* salt separated in needles (Found : N, 6.1; equiv., 234.9.  $\text{C}_7\text{H}_5\text{O}_6\text{SN}$  requires N, 5.96%; equiv., 235.0).

*4-Sulpho-3-methoxybenzoic Acid* (I).—The sulpho-*m*-hydroxybenzoic acid (22 g. in 50 c.c. of water) was neutralised and treated alternately with 25% potassium hydroxide solution (500 c.c.) and methyl sulphate (80 c.c.) until the violet fluorescence disappeared; the mixture was then heated with potassium hydroxide in excess to hydrolyse the ester formed, neutralised with sulphuric acid, concentrated, and cooled. The filtered solution, when acidified with hydrochloric acid, gave *potassium hydrogen sulpho-m-methoxybenzoate* in rhombic plates, which were washed and recrystallised from water for analysis (yield, 23 g.) (Found for the hydrated salt : K, 13.5;  $\text{H}_2\text{O}$ , 6.5; equiv., 286.8, 288.2.  $\text{C}_8\text{H}_7\text{O}_6\text{SK} \cdot \text{H}_2\text{O}$  requires K, 13.6;  $\text{H}_2\text{O}$ , 6.3%; equiv., 288.1. Found for the anhydrous salt : K, 14.4.  $\text{C}_8\text{H}_7\text{O}_6\text{SK}$  requires K, 14.4%).

The *sodium hydrogen* salt, prepared by using sodium hydroxide, presented much difficulty in its separation, as it carried sodium chloride along with it and was not easily isolated by filtration. For analysis it was recrystallised several times from water, separating as a glossy microcrystalline mass (Found for the anhydrous salt : Na, 8.9.  $\text{C}_8\text{H}_7\text{O}_6\text{SNa}$  requires Na, 9.05%).

The *barium* salt : The above acid potassium salt was neutralised with ammonia, and the neutral solution treated with barium acetate solution. The precipitated barium salt, crystallised from water, formed transparent beady crystals containing  $4\text{H}_2\text{O}$ , of which  $3\text{H}_2\text{O}$  were easily removed at  $120^\circ$  (Found : Ba, 31.1; loss at  $120^\circ$ , 13.4.  $\text{C}_8\text{H}_6\text{O}_6\text{SBa} \cdot 4\text{H}_2\text{O}$  requires Ba, 31.3;  $3\text{H}_2\text{O}$ , 12.3%).

The barium salt, dissolved in water, was treated with the equivalent amount of sulphuric acid, and the filtered solution concentrated to a small bulk; *4-sulpho-3-methoxybenzoic acid* crystallised in long shining plates containing  $2\text{H}_2\text{O}$ , m. p.  $228^\circ$  (Found : S, 11.85; equiv., 133.5.  $\text{C}_8\text{H}_6\text{O}_6\text{S} \cdot 2\text{H}_2\text{O}$  requires S, 11.9%; equiv., 134).

*Fusion of 4-Sulpho-3-hydroxybenzoic Acid with Alkali*.—Finely powdered acid potassium or sodium sulpho-*m*-hydroxybenzoate (7 g.) was added to fused potassium hydroxide or sodium hydroxide (22 g.) in a nickel crucible at  $220^\circ$  and the mass was well stirred. When the temperature was raised gradually, considerable frothing was observed; at  $300^\circ$  the mass became a clear liquid, which was

further heated at  $310^{\circ}$  for  $\frac{1}{2}$  hour. The fused mass was dissolved in water and neutralised with sulphuric acid, and the filtered solution acidified and extracted with ether. The extract on evaporation left a residue which crystallised from water in needles (3 g.), m. p.  $199^{\circ}$  (Found: equiv., 153.8. Calc. for  $C_7H_6O_4$ : equiv., 154). The acid gave all the characteristic reactions of protocatechuic acid, showed no depression in melting point in admixture with this acid, and gave veratric acid, m. p.  $181^{\circ}$ , on methylation. It formed a diacetyl derivative, m. p.  $152^{\circ}$  (compare Herzig, *Monatsh.*, 1885, 6, 872).

*Fusion of 4-Sulpho-3-methoxybenzoic Acid with Alkali.*—Acid potassium 4-sulpho-3-methoxybenzoate (15 g.) was similarly fused at  $310^{\circ}$ , and the fused mass examined as described above. The ethereal extract gave a product, m. p.  $199^{\circ}$ , identical with protocatechuic acid (yield, 6 g.).

In other fusions the temperature was maintained at  $270^{\circ}$  and  $280^{\circ}$ , and the mass examined. The neutral solution after concentration was acidified with hydrochloric acid; acid potassium sulpho-*m*-hydroxybenzoate then crystallised in prismatic plates, showing in alkaline solutions the violet fluorescence of sulpho-*m*-hydroxybenzoic acid (Found: K, 14.2;  $H_2O$ , 6.5%; equiv., 274.0). The acid mother-liquor on extraction with ether gave some protocatechuic acid, which showed that in the fusion of sulpho-*m*-methoxybenzoic acid with alkali demethylation preceded the replacement of the sulpho-group by hydroxyl.

*4-Chlorosulphonyl-3-methoxybenzoyl Chloride.*—The anhydrous acid potassium salt of 4-sulpho-3-methoxybenzoic acid (I) (15 g.) was triturated with phosphorus pentachloride (35 g.) and heated on a water-bath for 5 hours. The mixture became syrupy and hydrogen chloride was copiously evolved. The mixture was poured into ice-water and the insoluble portion was washed and dried (yield, 14 g.). The substance gradually changed in cold water, and in boiling water was readily hydrolysed to 4-sulpho-3-methoxybenzoic acid. It dissolved freely in benzene and toluene and moderately readily in carbon tetrachloride. *4-Chlorosulphonyl-3-methoxybenzoyl chloride* separated in rectangular plates, m. p.  $87^{\circ}$  (Found: S, 11.8; Cl, 26.15.  $C_8H_6O_4Cl_2S$  requires S, 11.9; Cl, 26.4%).

*4-Chlorosulphonyl-3-methoxybenzoic Acid.*—Finely powdered 4-chlorosulphonyl-3-methoxybenzoyl chloride (8 g.) was shaken with cold water (800 c.c.), the course of the hydrolysis being followed by the rise observed in the melting point of the product. After 8 days, the residue, which consisted solely of 4-chlorosulphonyl-3-methoxybenzoic acid, m. p.  $214^{\circ}$ , was collected, washed, and dried (yield, 5 g.). The substance, which was sparingly soluble in all organic

solvents, crystallised from toluene in small plates [Found : S, 12·7; Cl, 14·1; equiv. (excess of NaOH solution and back-titration), 83·0.  $C_8H_7O_5ClS$  requires S, 12·8; Cl, 14·2%; equiv. (if  $SO_2Cl$  becomes  $-SO_3H$  and  $HCl$ ), 83·5].

4-Sulphonamido-3-methoxybenzamide was obtained in quantitative yield by heating finely powdered 4-chlorosulphonyl-3-methoxybenzoyl chloride (5 g.) with ammonia ( $d$  0·88; 50 c.c.) until the excess of ammonia was expelled. It crystallised from water in fine needles or plates, m. p.  $255^\circ$  (Found : S, 13·8; N, 12·2.  $C_8H_{10}O_4N_2S$  requires S, 13·9; N, 12·2%).

4-Sulphonamido-3-methoxybenzoic Acid (II).—(1) 4-Chlorosulphonyl-3-methoxybenzoic acid (3 g.) was dissolved in concentrated aqueous ammonia (30 c.c.), and the excess of ammonia expelled by boiling. The solution on acidification gave 2·9 g. of 4-sulphonamido-3-methoxybenzoic acid (II), m. p.  $290^\circ$  (decomp.).

(2) 4-Sulphonamido-3-methoxybenzamide (2 g.) was boiled under reflux with concentrated hydrochloric acid (20 c.c.) for 24 hours and the solid product after cooling was collected, washed, and dried (yield, 2 g.). It had m. p.  $290^\circ$  (decomp.) and was identical with that obtained in (1).

(3) Another method of preparation is described on p. 1300.

The sulphonamido-3-methoxybenzoic acid was readily soluble in methyl alcohol, ethyl alcohol and acetone, moderately readily soluble in hot water, and almost insoluble in benzene and toluene. It crystallised from 50% alcohol in small rhombic plates [Found : S, 13·8; N, 6·1; equiv. (excess of NaOH solution and back-titration), 115·2.  $C_8H_9O_5NS$  requires S, 13·85; N, 6·1%; equiv. (if  $SO_2-NH_2$  becomes  $SO_3H$  and  $NH_3$ ), 115·5].

4-Thiol-3-methoxybenzoic Acid (monothiovanillic acid).—4-Chlorosulphonyl-3-methoxybenzoic acid (5 g.) was treated with tin (15 g.) and hydrochloric acid (40 c.c.) in the cold. After 2 hours the mixture was heated on a water-bath until the tin had dissolved. Excess of hydrochloric acid was then added and, after cooling, the solid, which floated on the surface, was collected, washed with dilute hydrochloric acid, dried (yield, 4 g.), and purified by repeated dissolution in sodium hydroxide and precipitation with hydrochloric acid. The acid dissolved readily in almost all organic solvents but with difficulty in water. It separated from dilute alcohol in microcrystalline form, m. p.  $180^\circ$  (Found : S, 17·3.  $C_8H_8O_3S$  requires S, 17·4%).

3-Methoxybenzoic Acid 4-Disulphide.—4-Chlorosulphonyl-3-methoxybenzoic acid (1 g.) was dissolved in alcohol and reduced with zinc dust (1·5 g.) and hydrochloric acid (10 c.c.) in the cold. After removal of the excess of zinc dust the clear liquid was treated with

solid ferric chloride in presence of hydrochloric acid and kept for 1 hour. The *disulphide*, which separated on dilution with water, was washed, dissolved in aqueous sodium carbonate, and reprecipitated with hydrochloric acid; it then crystallised from dilute alcohol as a fine white powder (0.9 g.), m. p.  $270^{\circ}$ , to a dark red liquid after softening at  $250^{\circ}$  [Found: equiv., 181.8.  $(C_8H_7O_3)_2S_2$  requires equiv., 183].

4-Methylthiol-3-methoxybenzoic acid (monothioveratric acid) was prepared from the thiol acid (3 g.), 25% sodium hydroxide solution (40 c.c.), and methyl sulphate (6 c.c.) in the usual way. A sodium salt which separated in short silky needles redissolved on addition of water. The solution on acidification gave a flocculent mass, which crystallised readily from all organic solvents, except chloroform and carbon tetrachloride, in lustrous needles (3 g.), m. p.  $193^{\circ}$  (Found: S, 16.1; equiv., 197.8.  $C_9H_{10}O_3S$  requires S, 16.2%; equiv., 198.0).

3-Methoxybenzoic Acid 4-Methylsulphone (V).—4-Methylthiol-3-methoxybenzoic acid (2 g.) was dissolved in aqueous sodium hydroxide and treated with 5% potassium permanganate solution on a boiling water-bath until the purple colour persisted. After addition of a little alcohol and filtration, the solution was concentrated to a small bulk and acidified; 3-methoxybenzoic acid 4-methylsulphone then separated in well-defined plates (1.9 g.), m. p.  $227^{\circ}$ , which were recrystallised from dilute alcohol (Found: S, 13.9; equiv., 230.1.  $C_9H_{10}O_5S$  requires S, 13.9%; equiv., 230.0). The sulphone is readily soluble in alcohol and acetone, moderately easily soluble in hot water, and almost insoluble in benzene, toluene, chloroform, and carbon tetrachloride.

[With Mr. C. T. BHATT.] 3-Methoxytoluene-4-sulphinic Acid (III) and 3-Methoxytoluene-4-sulphonic Acid.—These were prepared by following the experimental work of Haworth and Lapworth (*loc. cit.*). *m*-Cresol was nitrated by Staedel's method (*Annalen*, 1883, 217, 49; 1890, 259, 208) and 4-nitro-*m*-cresol, m. p.  $56^{\circ}$ , was separated from its 6-isomeride by distillation with steam. 4-Nitro-*m*-cresol thus obtained was dissolved in xylene, treated with potassium carbonate and methyl sulphate and converted into 4-nitro-3-methoxytoluene (m. p.  $61^{\circ}$ ) by heating under reflux for 20 hours. The methyl ether on reduction with stannous chloride and hydrochloric acid produced 4-amino-3-methoxytoluene, which was distilled with steam, diazotised, and treated with sulphur dioxide in presence of finely divided copper, all the necessary precautions suggested by Haworth and Lapworth in the conversion of diazo-salt into sulphinic acid being taken.

3-Methoxytoluene-4-sulphinic acid (III), which crystallised in

long needles, m. p.  $111^{\circ}$ , was digested with barium carbonate, and its barium salt oxidised with 1% barium permanganate solution. The barium 3-methoxytoluene-4-sulphonate which was thus held in solution was recovered and treated with the equivalent of potassium carbonate to give the corresponding potassium salt. The anhydrous potassium salt when digested with phosphorus pentachloride gave 3-methoxytoluene-4-sulphonyl chloride, m. p.  $79^{\circ}$ , which on treatment with ammonia produced 3-methoxytoluene-4-sulphonamide (IV), m. p.  $169^{\circ}$ . Haworth and Lapworth give  $79^{\circ}$  and  $168^{\circ}$  respectively.

*4-Sulpho-3-methoxybenzoic Acid (I) from 3-Methoxytoluene-4-sulphinic Acid (III).*—The above potassium 3-methoxytoluene-4-sulphonate, prepared from 3-methoxytoluene-4-sulphinic acid (III) (5 g.), was oxidised with 5% permanganate solution. After the manganese dioxide had been removed, the filtrate was concentrated and acidified with hydrochloric acid; the characteristic acid potassium 4-sulpho-3-methoxybenzoate, then obtained in well-shaped rhombic plates (3 g.), was recrystallised from water (Found: K, 13.5;  $H_2O$ , 6.35%; equiv., 287.5). This salt was successively converted into 4-chlorosulphonyl-3-methoxybenzoyl chloride, m. p.  $87^{\circ}$ , 4-chlorosulphonyl-3-methoxybenzoic acid, m. p.  $214^{\circ}$ , 4-sulphonamido-3-methoxybenzamide, m. p.  $255^{\circ}$ , and 4-sulphonamido-3-methoxybenzoic acid, m. p.  $290^{\circ}$  (decomp.), which were identical with those prepared from sulpho-*m*-hydroxybenzoic acid methyl ether (I).

*4-Sulphonamido-3-methoxybenzoic Acid (II) from 3-Methoxytoluene-4-sulphonamide (IV).*—3-Methoxytoluene-4-sulphonamide (IV) (2 g.) was oxidised with 5% potassium permanganate solution and the filtered liquid was concentrated and acidified with hydrochloric acid. 4-Sulphonamido-3-methoxybenzoic acid crystallised in small rhombic plates (1.8 g.) which, alone or mixed with specimens obtained by the two methods already described, melted and decomposed at  $290^{\circ}$  (Found: equiv., 115.4)\*.

*4-Thiol-3-methoxytoluene.*—3-Methoxytoluene-4-sulphinic acid (III) (5 g.) was reduced with tin (15 g.) and hydrochloric acid (40 c.c.) by the method described on p. 1298. 4-Thiol-3-methoxytoluene, isolated by steam-distillation and extraction with ether, was obtained as a colourless oil (4 g.), b. p.  $254^{\circ}$ , readily soluble in organic solvents (Found: S, 20.7.  $C_8H_{10}OS$  requires S, 20.8%). In alcoholic solution it gave with mercuric chloride a white mercaptide and with lead acetate a canary-yellow mercaptide [Found: Pb, 40.1.  $(C_8H_9OS)_2Pb$  requires Pb, 40.4%]. The benzoyl derivative, prepared by shaking an alkaline solution of 4-thiol-3-methoxytoluene with benzoyl chloride, crystallised from dilute methyl alcohol in



thin plates, m. p.  $76^{\circ}$ . The disulphide separated readily when a solution of iodine in potassium iodide was added to a solution of the mercaptan in sodium hydroxide; it crystallised from methyl alcohol in prismatic plates, m. p.  $83^{\circ}$ .

4-Methylthiol-3-methoxytoluene.—The above mercaptan (3 g.), dissolved in 25% sodium hydroxide solution (30 c.c.), was heated with methyl sulphate (6 c.c.) on a water-bath for 2 hours. The methylthiol, which separated as an oil and was extracted with ether, had an aromatic odour and boiled at  $269\text{--}270^{\circ}$  (yield, 3 g.) (Found: S, 19.0.  $\text{C}_9\text{H}_{12}\text{OS}$  requires S, 19.0%). When oxidised with hot alkaline 5% potassium permanganate solution, it was converted into 3-methoxybenzoic acid 4-methylsulphone, which, alone or mixed with the specimen described above, melted at  $227^{\circ}$  (Found: S, 13.8%; equiv., 229.6).

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# CLXV.—The Action of Substituted Aromatic Amines on Camphoric Anhydride. Hydroxy-, Methoxy-, and Ethoxy-camphoranic Acids and Camphoromethoxy- and -ethoxy-phenylimides.

By MAHAN SINGH and RAM SINGH.

THE work on the effect of the substituents on the rotatory powers of substituted camphoranic acids and camphorophenylimides (J., 1925, 127, 1966; 1927, 1944; 1928, 2410) has been extended to include 2'- and 4'-hydroxy-, -methoxy-, and -ethoxy-camphoranic acids and the corresponding phenylimides.

Table I records the values of  $[M]_D$  for the 2'- and the 4'-substituted camphoranic acids in the four solvents formulated. In every case

TABLE I.

2'-Substituent.	MeOH.	EtOH.	Me <sub>2</sub> CO.	MeEtCO.
OH .....	-37°	-47°	-45°	-53°
OMe .....	+30	+28	-16	-10
OEt .....	-50	-62	-90	-89
4'-Substituent.				
OH .....	+246°	+266°	+154°	+203°
OMe .....	+163	+152	+122	+99
OEt .....	+180	+154	+116	+104

the 4'-substituted compound exceeds the 2'- in molecular rotatory power. The relative influence of the substituents on the rotatory power is in the order OEt > OH > OMe for the 2'- and OH > OEt > OMe for the 4'-substituted acids. Methoxyl, which in the

2'-position produces an exceptionally large depression (compare Bretscher, Rule, and Spence, J., 1928, 1493), stands at one end of the polar series, carboxyl being at the other. Ethoxyl, instead of occupying a position near methoxyl, follows iodine in the polar series: this position is also indicated by the values of the acid/imide ratio (see J., 1928, 2411) for the phenetidines (see below).

The rotatory powers of cyclic compounds are generally greater than those of the corresponding open-chain derivatives, but the camphoranilic acids and the camphorophenylimides are exceptions to the rule (Wootton, J., 1910, 97, 405; see also Singh and Puri, J., 1926, 504). Wootton has cited the cases of  $\alpha$ -naphthyl and *o*-bromophenyl derivatives of camphoranilic acid, where the molecular rotatory powers of the imides are greater than those of the corresponding acids. It has, however, been shown (Singh, Ahuja, and Lal, J., 1928, 2410) that the *o*-bromo-acid prepared by Wootton was impure and that the pure acid has  $[M]_D = -61^\circ$  (in acetone) and not  $-41^\circ$ . Examples are now given in camphoro-*o*-methoxyphenylimide and camphoro-*o*-ethoxyphenylimide (in methyl alcohol and in ethyl alcohol) which have greater rotatory powers than the corresponding acids.

#### EXPERIMENTAL.

Camphoric anhydride was condensed with the hydroxy-, methoxy-, and ethoxy-anilines by the general method (J., 1928, 2410). The condensations were carried out at different temperatures to ascertain the effect of temperature on the acid/imide ratio.

*2'-Hydroxycamphoranilic Acid*.—The condensation product, which had a repulsive odour, was dissolved in alcohol, water was added, and the precipitated oil was removed and extracted with dilute sodium bicarbonate solution. The reddish-brown extract on acidification with dilute acetic acid gave the camphoranilic acid as a gummy mass. A solution of this in aqueous ammonia was boiled with animal charcoal and filtered, and the acid reprecipitated. *2'-Hydroxycamphoranilic acid* finally separated from an alcoholic solution (charcoal), after addition of a little water, in minute prisms, m. p.  $183^\circ$  after shrinking at  $159^\circ$  (Found: N, 4.9.  $C_{16}H_{21}O_4N$  requires N, 4.8%).

*4'-Hydroxycamphoranilic acid* crystallised from dilute alcohol in deep violet prisms, which gave a light grey mass when powdered; m. p.  $241-242^\circ$  (Wootton, *loc. cit.*, gives m. p.  $239^\circ$ ) (Found: N, 4.9. Calc.: N, 4.8%).

*2'-Methoxycamphoranilic Acid and Camphoro-*o*-methoxyphenylimide*.—The condensation was carried out at  $125^\circ$ , at  $140^\circ$ , and at  $150^\circ$ : the yield of imide was 38–40% at  $150^\circ$ .

The *acid* crystallised from dilute alcohol in small plates, m. p. 152° after shrinking at 141° (Found: N, 4.8; equiv., 309.  $C_{17}H_{23}O_4N$  requires N, 4.6%; equiv., 305). The *imide* crystallised in needles, m. p. 136° (Found: N, 4.9.  $C_{17}H_{21}O_3N$  requires N, 4.9%). The acid is more soluble than the imide in the usual organic solvents.

4'-Methoxycamphoranilic acid formed colourless prismatic needles, m. p. 204° (Found: N, 4.7%; equiv., 303).

Camphoro-p-methoxyphenylimide separated from alcohol in needles, m. p. 122—123° (Found: N, 5.0%). The following yields were obtained: at 120°, 0; at 140°, trace; at 150°, 33—34%; above 200°, 100%.

2'-Ethoxycamphoranilic Acid and Camphoro-o-ethoxyphenylimide.—The *acid* crystallised in short prismatic needles, m. p. 146—147° (Found: N, 4.5; equiv., 319.  $C_{18}H_{25}O_4N$  requires N, 4.4%; equiv., 319).

The *imide*, obtained by heating the condensation mixture at 220° for 1½ hours or by Wootton's method (*loc. cit.*), melted at 138° (Found: N, 4.7.  $C_{18}H_{25}O_3N$  requires N, 4.65%). The yield of the imide was: at 125°, 0; at 140°, 0; at 150°, very small; above 200°, 100%.

4'-Ethoxycamphoranilic Acid and Camphoro-p-ethoxyphenylimide.—The *acid* crystallised in small thick prisms, m. p. 202—203° (Found: N, 4.5%; equiv., 316).

The *imide* crystallised from alcohol in thin needles, m. p. 122° (Found: N, 4.7%). The yield was negligible at 125° and at 140° and 27% at 150°.

If anisidine and phenetidine compounds are heated too rapidly in the combustion tube during analysis, methane is evolved (compare Forster, J., 1909, 95, 952).

TABLE II.

Rotatory Powers of Hydroxy-, Methoxy-, and Ethoxy-camphoranilic Acids and of the Corresponding Imides ( $l = 2$ ).

Solvent.	Camphoranilic Acids.					
	Conc. (g./25 c.c.).	$[\alpha]_D$ .	Conc. (g./25 c.c.).	$[\alpha]_D$ .	Conc. (g./25 c.c.).	$[\alpha]_D$ .
	2'-Hydroxy-.		4'-Hydroxy-.		2'-Methoxy-.	
MeOH .....	0.1385	-12.6°	0.1242	+84.5°	0.2183	+9.7°
EtOH .....	0.1450	-16.2	0.1200	+91.6	0.2201	+9.0
Me <sub>2</sub> CO .....	0.1427	-15.4	0.1251	+52.9	0.3268	-5.3
MeEtCO .....	0.1564	-18.5	0.1290	+69.8	0.4390	-3.1
	4'-Methoxy-.		2'-Ethoxy-.		4'-Ethoxy-.	
MeOH .....	0.2671	+53.3	0.4161	-15.6	0.2465	+56.3
EtOH .....	0.2570	+49.9	0.4220	-19.5	0.2504	+48.3
Me <sub>2</sub> CO .....	0.2491	+40.1	0.4498	-28.3	0.2559	+36.4
MeEtCO .....	0.2757	+32.7	0.4144	-28.0	0.2459	+32.6

## Camphorophenylimides.

	Conc. (g./25 c.c.).	$[\alpha]_D$ .	$[M]_D$ .	Conc. (g./25 c.c.).	$[\alpha]_D$ .	$[M]_D$ .
		o-Methoxy-.			p-Methoxy-.	
MeOH ...	0.2638	+17.1°	49°	0.2515	+29.3°	84°
EtOH .....	0.2427	+14.9	43	0.3437	+21.8	63
Me <sub>2</sub> CO ...	0.2657	+14.1	40	0.2561	+17.0	49
MeEtCO ...	0.2628	+15.3	44	0.2724	+11.9	34
		o-Ethoxy-.			p-Ethoxy-.	
MeOH ...	0.1205	+38.1	115	0.2461	+23.4	86
EtOH .....	0.1257	+32.6	98	0.3429	+15.6	47
Me <sub>2</sub> CO ...	0.1201	+26.6	80	0.2461	+17.7	53
MeEtCO ...	0.1256	+25.4	77	0.2553	+13.0	39

The readings were taken in a 2-dcm. tube at 23° within 30 minutes of making up the solution. There was no mutarotation.

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# CLXVI.—The Validity of the Interference Method for the Measurement of the Specific Area of a Copper Surface.

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THE surfaces of all solids are rough, and possess irregularities of both microscopic and macroscopic dimensions: even optically plane surfaces probably contain roughnesses of a molecular order. In general, therefore, the specific area of a surface will be very different from its apparent area. Of the methods proposed for the measurement of the specific area, those due to Bowden and Rideal (*Proc. Roy. Soc.*, 1928, A, **120**, 80), Constable (*ibid.*, 1927, A, **115**, 570), and Wilkins (*Nature*, 1930, **125**, 236) are particularly suitable for use with metals. Bowden and Rideal calculate the specific area from the amount of hydrogen which must be deposited upon an electrode in order to bring about a given change of potential, as compared with the amount required to bring about the same change of potential at a liquid mercury electrode. Wilkins has pointed out that the specific area may be measured if the vapour pressure and rate of vaporisation of the surface are known. Constable's method is entirely different, however; having shown that the colour of the oxide film formed on metals, such as nickel, copper, and iron, is due to interference and is consequently determined uniquely by its thickness, he calculates the volume of a film from its weight and the density of the oxide, and combines this with its thickness, as determined by its colour, to estimate the specific area of the surface.

It is difficult to compare results obtained by these three methods. Bowden and Rideal measure the area accessible to hydrated hydrogen ions, and Wilkins measures that accessible to condensing atoms of the vaporising solid; thus these two methods should give similar results, and although the experimental evidence to which the latter method can be applied is at present scanty, yet the respective results are not contradictory. The relation between the results obtained by these methods and that of Constable is much more complex. In the particular case of an activated nickel surface, the results obtained by Constable and by Bowden and Rideal are widely different. The former (*Proc. Roy. Soc.*, 1928, A, **119**, 196) finds that the ratio ( $A$ ) of the specific to the apparent area is 1.3—4.5, depending upon the degree of activation of the surface, while the other workers obtain the much higher value of 46 for a recently activated surface, and 29 for the same surface after it has been allowed to "age." Bowden (*Nature*, 1928, **122**, 647), discussing the difference between these figures, has pointed out that the interference method is unable to take account of irregularities which are of an order less than  $10^{-5}$  cm. It would appear, therefore, that these minute irregularities are able to increase the specific area by a factor of at least 10.

During the course of a study of the kinetics of the oxidation of copper, an opportunity arose for the application of the interference method to this metal. Constable, while providing the necessary optical data for this case, has studied only nickel in detail. It is clearly important that the values of  $A$  obtained for nickel should be confirmed (as far as order of magnitude is concerned) by experiments on another metal, so that the reality of the ten-fold factor may be substantiated.

#### EXPERIMENTAL.

The copper was used as pieces (1 sq. dm. in area) of pure electrolytic foil which had been carefully cleaned by abrasion first with emery paper of gradually increasing fineness and finally with Hubert 000. It was further cleaned by rubbing with cotton-wool dipped in alcohol and then with dry grease-free cotton-wool. The oxidations were carried out by heating either in air or in a closed system of known volume containing pure oxygen. In the first case, the amount of oxide formed was determined by weighing the copper before and after oxidation on a Sartorius microbalance; in the second, the weight of oxide was determined from the fall of pressure in the system. The pressures were determined accurately by measuring the movement of a mercury column with a travelling microscope. Activation of the copper was brought about by reduction with hydrogen. A detailed account of the experimental technique will appear in a forthcoming paper.

*Results.*

(1) *Values of A for Copper Surfaces which have not been activated.*—The first series of experiments refers to the oxidation of copper foil at 183°. The results are shown in Table I in the order of increasing film thickness. In all the tables, weights of oxide are given as mg. per sq. dm. The figures of column 2 were determined from the colour of the oxide film, Constable's data being used to correlate this with the thickness (see *Proc. Roy. Soc.*, 1928, A, 119, 196).

TABLE I.

Wt. of oxide.	Wt. of oxide, from colour.	Ratio, A.
2.22	5.01	0.443
2.54	5.18	0.490
3.64	5.76	0.632
3.82	5.88	0.65
4.56	7.23	0.63

TABLE II.

Temp. of oxidation.	Wt. of oxide.	Wt. of oxide, from colour.	Ratio, A.
125°	0.843	2.47	0.341
150	1.73	2.82	0.614
175	3.37	5.41	0.623
200	5.68	7.41	0.767

All the experiments give anomalous values of  $A$ , a value of less than unity being physically impossible, since it suggests that the specific area is less than the apparent area.

In order to confirm the result, Vernon's data (J., 1926, 2273) were used for the calculation of  $A$  (see Table II). The figures of Tables I and II are in complete agreement, showing that over the experimental range  $A$  is always less than unity, and increases as the temperature of oxidation and the thickness of the oxide film increase. The thickness of the surface film containing oxide does not, therefore, determine uniquely the colour of the film. In an attempt to obtain further information, a few determinations of  $A$  were made with activated copper surfaces, for all Constable's work has been carried out on activated metallic surfaces.

(2) *Values of A for Activated Copper Surfaces.*—The first experiments were made with a sample of copper which had been oxidised and reduced many times until it had reached a state of maximum activation. The results were :

Temp. of oxidation .....	183°	305°
Wt. of oxide .....	3.61	5.00
Wt. of oxide, from colour .....	2.24	2.53
A .....	1.62	1.98

The change in the value of  $A$  given by the experiment at 305° is particularly interesting. The reduction after the first experiment was carried out at 183°. Since the subsequent oxidation at 305° required only a few minutes, the deactivation accompanying it must have been slight. The increase in  $A$  is therefore to be attributed solely to the increase in the temperature of oxidation. This phenomenon was confirmed in a second series of experiments in

which  $A$  was determined for a specimen of copper during a period of gradually increasing activation (see Table III). The value of  $A$  seems to be dependent chiefly upon the temperature of oxidation—at least, to such an extent as to mask any changes due to activation.

TABLE III.

No. of expt.	Temp. of oxidn.	No. of oxidns. after reduction.	Wt. of oxide.	Wt. of oxide, from colour.	$A$ .
1	305°	2	5.79	2.71	2.14
2	305	3	5.39	2.53	2.13
3	183	4	4.92	3.44	1.43
4	183	6	4.01	2.94	1.37
5	183	20	4.35	2.53	1.72
6	183	21	4.47	2.53	1.76

Expt. 1 was carried out on a piece of copper which had been already oxidised once and reduced at 305°. The activation of the surface gives a value of  $A$  greater than unity and of the order of those obtained by Constable in his work. The oxide film formed in this experiment was reduced at 305°. Notwithstanding the increase of activation (as measured by the increased rate of oxidation) between Expts 1. and 2, any change in the value of  $A$  was smaller than the experimental error, which is about 0.1 unit. Even more striking is the value of the ratio obtained from Expt. 3. Before this oxidation, the oxide film had been reduced at 183°, and reduction at this low temperature should be accompanied by a considerable increase in area owing to the decrease in the sintering of the surface. Instead of an increase in  $A$ , however, an unexpected decrease was obtained. Subsequent activation at 183° gave at the terminal state (see Expts. 5 and 6) values in reasonable agreement with that of the first experiment in the previous series (p. 1306).

#### Discussion.

The experimental results may be summarised by saying that copper which has not been activated gives anomalous values for  $A$ , which are dependent upon the temperature and the thickness of the oxide film; further, while the values of  $A$  given by activated copper are greater than unity, they are also very largely dependent upon the temperature of heating, and are scarcely affected by the activation of the surface.

The interference theory of the colours of thin films of oxide on metals seems to be well established qualitatively (see, *e.g.*, Evans, J., 1925, 127, 2484; *Proc. Roy. Soc.*, 1925, A, 107, 228; *Chem. and Ind.*, 1926, 45, 213). Constable's work provides the chief quantitative evidence in its favour, in that he has shown that if the quantity of oxide determined directly is corrected by an area factor ( $A > 1$ ) it is equal to the quantity of oxide given by the colour of the film.

This work has shown, however, that in the case of copper, the nature of the correcting factor  $A$  is not so simple as Constable has supposed. In order to interpret the anomalies two courses are open, *viz.*, (a) to reject the interference theory as an explanation of the colours; (b) to amend the calculations of Constable. In view of the qualitative evidence in favour of the interference theory, the second course would seem to be the more hopeful.

Experiments on the kinetics of the low-temperature oxidation of copper (shortly to be published; compare also Wilkins, *Z. Elektrochem.*, 1929, **35**, 500) have shown that oxygen diffuses through the oxide film to the underlying copper along the grain boundaries of the oxide. The oxidation of copper appears, therefore, to proceed grain by grain; and it is to be expected, in consequence of this granular oxidation, that the oxide film will contain appreciable quantities of unchanged copper. Further, one would expect the proportion of unchanged copper in the film to be the greater the larger the grain size of the copper and the thinner the film. Direct experimental evidence demonstrating the existence of this unchanged copper has been recently obtained by Evans and Stockdale (J., 1929, 2651), who heated a square sheet of copper along one edge, obtaining a film of oxide of thickness gradually decreasing as the distance from the hot edge is increased. They found that the thin oxide films formed at the low-temperature points contained "much residual metallic copper"; the proportion of metallic copper to oxide gradually diminished as the high-temperature edge was approached.

An explanation of the experimental results is now possible on the basis that the colour of the oxide films is an interference phenomenon. Copper which has not been activated is made up of large grains. The film which gives rise to the colour will not, therefore, be pure oxide, but will contain large amounts of unchanged metal. The volume of the film as calculated by Constable's method will consequently be much too great, and values of  $A$  will be obtained which are less than unity. The gradual increase in  $A$  with increasing film thickness is in perfect agreement with this interpretation.

Activated copper, on the other hand, has a much smaller grain size, and the oxide films formed by it will contain less unchanged copper. Further, the proportion of unchanged copper will, as before, be smaller the higher the temperature.

We therefore conclude that, as far as copper is concerned, Constable's interference method possesses very narrow limitations; for it is clear that, if results of accuracy are to be obtained, one must determine the optical properties and the density of each film.



This restriction will not apply to nickel, for Evans and Stockdale (*loc. cit.*) have shown that its oxide films are remarkably free from metallic occlusions. The values of  $A$  for this metal determined by the interference method are trustworthy. Further, although the values of  $A$  found in this work for activated copper are not a true indication of the specific area, they are of such a nature that they may be said to confirm, as far as order of magnitude is concerned, the results of Constable for activated nickel. The remarkable increase of  $A$  when determined with the hydrogen-ion method is therefore real; and the irregularities of dimensions less than  $10^{-5}$  cm. would appear to increase the specific area by as much as ten times.

*Summary.*

It is shown that, when Constable's interference method for the measurement of the specific area of a surface is applied to oxide films formed on copper which has not been activated, the values obtained for the ratio ( $A$ ) of the specific to the apparent area are anomalous in that they are always less than unity. Further,  $A$  is not a constant for a given surface but increases with the thickness of the oxide film and the temperature of oxidation. Activation of the copper surface by oxidation and reduction gives values of  $A$  which are greater than unity but are still dependent upon the temperature of oxidation. The interference method, therefore, does not give trustworthy values for the specific area when applied to the measurement of copper surfaces.

It is suggested that these results may be explained by assuming that the oxide film contains unchanged metallic occlusions, the proportion of unchanged metal to oxide varying with the conditions and extent of oxidation. Experimental evidence is cited in favour of this interpretation.

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CLXVII.—*The Lower Trialkyl Orthophosphates.*  
*Part I.*

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ALTHOUGH fairly complete information respecting some of the physical properties of trimethyl and triethyl orthophosphates is available, little is known concerning those of the other lower alkyl orthophosphates. Boiling points and densities of tri-*n*-propyl, triisopropyl, and triisobutyl phosphates have been recorded, but tri-*n*-butyl and tri-*n*-amyl orthophosphates have not hitherto been prepared. The preparation and properties of several phosphoric esters have been recently described by Plimmer and Burch (J., 1929, 279, 292). The present series of investigations is confined to the determination of certain physical constants of the lower trialkyl phosphates from methyl to amyl. In view of the paucity and the conflicting character of the results hitherto recorded concerning the physical properties of the phosphoric esters, it was considered advisable to carry out new measurements.

EXPERIMENTAL.

The phosphates were prepared by the action of phosphorus oxychloride on the sodium alkoxides. For instance, in the preparation of tri-*n*-butyl orthophosphate, sodium *n*-butoxide was first made by adding gradually 46 g. of sodium to 600 c.c. of *n*-butyl alcohol and then distilling off the excess of alcohol under reduced pressure. To the butoxide, 200 c.c. of dry ether were added, and 60 c.c. of phosphorus oxychloride in 100 c.c. of ether were run in with ice-cooling. The mixture was then boiled gently for an hour, water added, and the ethereal layer separated and dried over anhydrous sodium sulphate. The ether having been expelled, the residual liquid was distilled under 50 mm. pressure, 70 g. of ester being thus obtained. It was purified by several redistillations [Found: P, 11.9.  $(C_4H_9)_3PO_4$  requires P, 11.7%]. Tri-*n*-amyl orthophosphate was prepared in a similar way [Found: P, 10.0.  $(C_5H_{11})_3PO_4$  requires P, 10.1%].

The determination of phosphorus in these esters was effected gravimetrically by oxidation with a mixture of concentrated nitric and sulphuric acids, neutralisation with ammonia, and precipitation with ammonium molybdate.

On being distilled, even under 5 mm. pressure in the absence of air, tri- $\beta$ -methylbutyl, tri- $\gamma$ -methylbutyl, and tri-*n*-hexyl orthophosphates decomposed, whilst the tri-*n*-amyl ester gave distinct

indications of decomposition on being distilled under 150 mm., and, similarly, tri-*n*-butyl phosphate under 760 mm.

The lower trialkyl orthophosphates, with the exception of the methyl and ethyl members, are incompletely miscible with water at the ordinary temperature, but they mix in all proportions with alcohol, ether, or benzene. The methyl ester possesses a buttery smell, the ethyl a sharp apple-like one, whilst the propyl, butyl, and amyl esters have musty, but pleasant, odours. The *n*-butyl and *n*-amyl phosphates were very slightly yellowish, the colour apparently indicating incipient decomposition.

The boiling points under 50 mm., 100 mm., and 150 mm. were determined in an apparatus which permitted of the constant maintenance of any low pressure by means of a controllable air-leak into a reservoir in conjunction with a "Hyvac" air-pump. Thermometers and barometers standardised at the National Physical Laboratory were employed, and all necessary corrections were applied. In the determinations of density, weighings were corrected for displacement of air. The coefficients of thermal expansion,  $\alpha$ , have been calculated by means of the formula,

$$\alpha = (d_4^{25^\circ} - d_4^{40^\circ}) / (40d_4^{40^\circ} - 25d_4^{25^\circ}).$$

TABLE I.

*Boiling Points, Densities, and Coefficients of Thermal Expansion of Trialkyl Orthophosphates.*

Phosphate.	B.p. under given pressure (mm.Hg).					$d_4^{25^\circ}$ .	$d_4^{40^\circ}$ .	$\alpha \times 10^5$ .
	10	50	100	150	760			
Methyl	73°	110°	129°	142°	196°	1.2052	1.1872	104
Ethyl	90	128	148	159	215	1.0637	1.0490	96
<i>n</i> -Propyl	121	161	180	193	252	1.0023	0.9884	96
<i>n</i> -Butyl	150	196	211	227	289	0.9727	0.9596	93
<i>iso</i> Butyl	138	177	196	209	264	0.9617	0.9483	96
<i>n</i> -Amyl	—	225	—	—	—	0.9497	0.9373	90

When plotted against temperature, the present values of the density of the methyl ester agree with those of Weger (*Annalen*, 1883, **221**, 89) at 0° and of Cavalier (*Bull. Soc. chim.*, 1898, **19**, 887; *Ann. Chim. Phys.*, 1899, **18**, 460) at 15°, but not with the values given by Arbusov (*J. Russ. Phys. Chem. Soc.*, 1907, **38**, 161) and by Drushel (*Amer. J. Sci.*, 1915, **40**, 643). Similarly, in the case of the ethyl ester the present values are in fair agreement with those given by Zecchini (*Gazzetta*, 1894, **24**, 34) for 28.1°, by Arbusov for 19°, by Arbusov and Ivanov (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 2015) for 20°, and by Sugden, Reed, and Wilkins (*J.*, 1925, **127**, 1538) for 15° and 38°, but not with those of Cavalier and of Limpricht (*Annalen*, 1865, **134**, 347). The present results accord fairly well

with those of Arbusov and of Drushel for tri-*n*-propyl phosphate, and of Drushel for triisobutyl phosphate at 22°.

In the series of normal phosphates, the average increase in molecular volume from one member to its next homologue is 17.4 c.c. per CH<sub>2</sub> group at 25°, and 17.7 c.c. at 40°. It is noteworthy that at 25° the average difference for a CH<sub>2</sub> group in the case of the lower fatty esters is also *ca.* 17.4 c.c., and at 40° *ca.* 17.5 c.c.

Throughout the range of pressure, *p*, from 10 mm. to 760 mm., the value of the boiling point, *t*°, given by the following equations agrees within an average error of 0.6° with our direct observations :

Methyl ester :	$8.1440 - \log_{10} p = 2468.4/(t + 273)$
Ethyl ester :	$8.3283 - \log_{10} p = 2658.4/(t + 273)$
<i>n</i> -Propyl ester :	$8.5188 - \log_{10} p = 2960.0/(t + 273)$
<i>n</i> -Butyl ester :	$8.5861 - \log_{10} p = 3206.5/(t + 273)$
<i>iso</i> Butyl ester :	$8.9945 - \log_{10} p = 3283.1/(t + 273)$

The boiling points under 10 mm. given in Table I have been calculated with these equations, and agree well with the direct measurements of Arbusov (*Ber.*, 1905, **38**, 1172) for trimethyl, tri-*n*-propyl and triisobutyl phosphates under this pressure. Further, the data of Drushel for the last two esters at 15 mm., and of Sugden, Reed, and Wilkins for the triethyl compound at 25 mm., are confirmed by the above equations, but all the boiling points given by Cavalier are too low.

The corresponding values of the molar latent heat of vaporisation are as follows: Trimethyl phosphate, 11,300 cal.; triethyl, 12,170 cal.; tri-*n*-propyl, 13,550 cal.; tri-*n*-butyl, 14,680 cal.; triisobutyl, 15,030 cal.

The refractive indices were measured with a Pulfrich refractometer, made by Wolz of Bonn, and an Abbé refractometer, by Hilger of London. Both instruments were standardised by the use of water and of benzene.

TABLE II.

*Refractive Indices of Trialkyl Orthophosphates.*

Phosphate.	$n_D^{25}$ .	$n_D^{20}$ .	$n_D^{25}$ .
Methyl .....	1.3990	1.3950	1.3934
Ethyl .....	1.4082	1.4039	1.4021
<i>n</i> -Propyl .....	1.4182	1.4136	1.4118
<i>n</i> -Butyl .....	1.4274	1.4224	1.4203
<i>iso</i> Butyl .....	1.4222	1.4173	1.4152
<i>n</i> -Amyl .....	1.4332	1.4283	1.4262

Previous investigators (Zecchini, *loc. cit.*; Arbusov and Ivanov, *loc. cit.*) have measured the refractive index of triethyl phosphate only; it is noteworthy that, on plotting their values for  $n_D$  and the present one against temperature, the points obtained all lie on a straight line. Further, the values of  $n_F$  and  $n_C$  for triethyl phosphate

given by Arbusov and Ivanov agree excellently with those found in the present work.

Owing to the circumstance that the values of the atomic refractivities of oxygen bound to phosphorus are unknown, it is impossible to calculate the atomic refractivity of phosphorus from the values of the molecular refractivities of the phosphoric esters. If it could be assumed that oxygen in an alkyloxy-group possessed the same refractivity as in an ether, use could be made of Lorentz-Lorenz refractivities, *e.g.*, those of Eisenlohr (*Z. physikal. Chem.*, 1910, **75**, 585), to calculate the value of the refractivity of the orthophosphoryl group,  $\text{OP:}$ . However, it appears preferable to derive a value for the refractivity of the orthophosphoric group,  $\text{OP(O)}_3$ , by deducting the values for carbon and hydrogen from the molecular refractivity of the ester. Values of the refractivity for this group so obtained are given in Table III, where they are denoted by the symbol  $[r_L]$ , values of molecular refractivity,  $(n^2 - 1)M/(n^2 + 2)d$ , being denoted by  $[R_L]$ .

TABLE III.

*Molecular and Group Refractivities.*

Trialkyl phosphate.	$[R_L]_f$ .	$[R_L]_b$ .	$[R_L]_c$ .	$[r_L]_f$ .	$[r_L]_b$ .	$[r_L]_c$ .
Methyl	28.119	27.869	27.769	10.770	10.715	10.702
Ethyl	42.263	41.870	41.706	10.910	10.862	10.848
n-Propyl	56.394	55.849	55.635	11.037	10.987	10.986
n-Butyl	70.336	69.616	69.312	10.975	10.900	10.872
iso-Butyl	70.383	69.666	69.358	11.022	10.950	10.918
n-Amyl	84.401	83.567	83.209	11.036	10.997	10.978
			Mean for $\text{PO}_4$	10.958	10.902	10.884

It is hoped that work, now in progress, on the optical properties of alkyl phosphites and of related compounds will help to elucidate the problem of the evaluation of the atomic refractivity of phosphorus when bound to oxygen.

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## CLXVIII.—*Studies in the Reactivity of Aromatic Hydroxyl Groups. Part I.*

By HAROLD LLEWELYN BASSETT.

THIS work has been undertaken with a view to investigate the influences affecting the reactivity of hydroxyl groups in aromatic compounds. Many investigations with the same general object have been carried out, and those most closely connected with the work now described are the determinations of velocity coefficient

by Panoff (*A.*, 1903, ii, 357) for the reaction between acetic anhydride and various phenols in benzene solution at 100°, and by Bernoulli and Goar (*Helv. Chim. Acta*, 1926, 9, 730) for the reaction between benzoyl chloride, or substituted benzoyl chlorides, and a number of phenols.

In the present case the reaction between phenols and acetyl bromide in ethyl acetate solution at 0° is used, and the half-periods of the reactions are obtained from a time-titration curve. The reciprocals of these half-periods are the comparative figures quoted.

A previous attempt on similar lines, using ether as solvent, failed owing to the ether unexpectedly taking part in the reaction (Bassett and Taylor, *J.*, 1929, 1568).

The half-periods obtained for the compounds studied (in minutes) were as follows: Phenol, 14.5 (1); *o*-cresol, 25.25 (0.574); *m*-cresol, 8.5 (1.71); *p*-cresol, 6.17 (2.35); thymol, 31 (0.468); carvacrol, 20 (0.725). The reciprocals of these figures, against phenol as unity, are given in parentheses. Panoff, and Bernoulli and Goar (*loc. cit.*), obtained similar results in the reactions which they studied, except that they found *m*-cresol to react slightly more rapidly than *p*-cresol. In all cases they found ortho-substituted phenols to react slowly.

The figures obtained in the present work do not depend upon the particular high concentrations chosen, since the ratio for phenol and thymol was found to be unchanged at half the concentration, although for some phenols the more dilute solution gives an inconveniently slow reaction.

While changes in the concentration of the phenol affect the rate of the reaction, material changes in the proportion of acetyl bromide (*e.g.*, 0.75, 1, 1.25 equivs. per equiv. of phenol) have no effect. This suggests that the reaction measured is not the simple bimolecular one, but that there is a preliminary rapid addition of the two reactants, followed by a slower unimolecular breakdown, which is the reaction actually measured. The point may be of importance, especially in connexion with the "ortho effect."

The effect of adding a little water to the reacting mixture is interesting. The titrations fell as though no water were present, but before reaching the lowest point they began to rise again, finally reaching a point nearly equal to the initial titration. It is evident, therefore, that when only a little water is present the formation of phenyl acetate proceeds almost to completion and is followed by a slower hydrolysis. This preferential reaction of acetyl bromide with phenol instead of with water is curious, since in the absence of phenol the reaction with water is very rapid. It may perhaps be connected with the above suggestion as to the rapid formation of an addition compound of phenol and acetyl bromide as the first stage

in the reaction. Such a course for the reaction had already been inferred from the work done with ethereal solutions (*loc. cit.*). It is proposed to carry out these determinations on a larger number of phenols, selected with a view to throw light on the problems involved.

#### EXPERIMENTAL.

The ethyl acetate was treated with acetyl chloride to remove final traces of alcohol, washed with sodium carbonate and water, dried, and distilled. The acetyl bromide was of A.R. quality, and was found to be of about 94% purity, the remainder being acetic acid and hydrogen bromide. For the purpose of calculating equivalents, it was treated as the pure substance, since it was shown that comparatively large variations in the amount of acetyl bromide had no effect on the half-period of the reaction. The phenols used were carefully purified and dried.

A determination was carried out by dissolving in ethyl acetate a weight of the phenol equivalent to 1 c.c. of acetyl bromide and making up the solution to 8 c.c. To this solution 1 c.c. of acetyl bromide was added after both had been brought to 0°. The mixture was well shaken and quantities of 1 c.c. were withdrawn at suitable intervals (commencing at 1 min. from the time of mixing), added to about 100 c.c. of water, and titrated with *N*/5-sodium hydroxide. The reaction was carried out in a small stoppered flask which was maintained at 0° throughout with crushed ice. The small quantities of liquid used permitted of very efficient cooling, and the 1 c.c. of the mixture withdrawn for each titration dissolved quickly and almost completely in about 100 c.c. of water, thus permitting practically instantaneous quenching of the reaction. Frequent shaking of the flask was necessary in order to secure uniform results. The infinity reading was usually taken on the following day, and was shown to be unchanged in the course of a further 24 hours. It was found most satisfactory to derive the zero titration from that taken at one minute, and a typical example is given. The half-periods quoted are the means of two or three concordant determinations.

#### *Carvacrol.*

Titration of 1 c.c. of the reaction mixture at stated intervals with 0.1945*N*-sodium hydroxide.

<i>t</i> (mins.) .....	1	4	7	10	16	26	∞
C.c. ....	15.3	14.5	13.95	13.35	12.55	11.55	8.65

Zero titration derived from curve = 15.6 c.c.

Half value = 12.125 c.c.

Half-period = 20 mins.

THE TATEM LABORATORIES, UNIVERSITY COLLEGE, CARDIFF.

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CLXIX.—*The Critical Solution Temperature of the System Methyl Alcohol-cycloHexane as a Means of detecting and estimating Water in Methyl Alcohol.*

By DAVID CHARLES JONES and SIMON AMSTELL.

THE sensitiveness to impurities of a critical solution temperature (*C.S.T.*), either binary or ternary, varies considerably with the impurity: in some cases the effects produced are very small, but in others they are so large as to constitute one of the most sensitive of the known criteria of liquid purity (J., 1923, 123, 1374, 1384).

It is now shown that the *C.S.T.* in the system methyl alcohol-cyclohexane is very sensitive indeed to the presence of water in the alcohol. This is of interest because, in many investigations, it is this impurity in the alcohol which it is necessary to detect and estimate from time to time. Moreover, the other common impurities are removable by chemical means and do not reappear in the alcohol. *cycloHexane* was chosen as the second component because it is readily obtained, can be purified easily, and has, in its melting point, a very sensitive criterion of its own purity.

EXPERIMENTAL.

*Preparation of Materials.*—*Methyl alcohol.* This was from two sources, commercial "absolute" and A.R. methyl alcohol (B.D.H.). Large quantities (2000 c.c. approx.) were fractionated through a ten-foot column of the type suggested by Clarke and Rahrs (*J. Ind. Eng. Chem.*, 1923, 15, 349), and the intermediate fractions (1500 c.c. approx.) subjected to the treatment of Bates, Mullaby, and Hartley (J., 1923, 123, 401) to remove acetone, and again fractionated through the column. The result is shown in Table I. Throughout the process of purification the dryness of the alcohol was tested by a miscibility temperature (*M.T.*) with pure *cyclohexane*, 69.15% of the latter being present. For the dry alcohol the value is 45.52°, very close to the *C.S.T.*; 0.01% of water in the alcohol produces a rise of 0.15°. The details of the determination of the miscibility temperature are described later.

TABLE I.

Fraction.	Vol., c.c.	<i>M.T.</i>	Water content, %, calc. ( $\pm 0.01\%$ ).	Alcohol content, %.
Original	2400	—	42 (app.)	58 (app.)
First	750	47.42°	0.12	99.88
Second	300	49.90	0.29	99.71
Third	200	52.28	0.48	99.52

These results show very clearly the efficiency of the ten-foot column. A 90% yield of the alcohol, containing less than 0.5% of



water, is obtained after one distillation from a solution originally containing 58% of alcohol. The acetone in the fractions was estimated as 0.002% by the method suggested by Bates, Mullaby, and Hartley (*loc. cit.*). The mercuric cyanide test for acetone (Hartley and Raikes, J., 1925, 127, 524) and Mayer's test for pyridine gave negative results.

In order to dry the alcohol, Fractions 2 and 3 (above) were mixed and treated with aluminium amalgam, following the procedure of Hartley and Raikes (*loc. cit.*). The alcohol was distilled off in an apparatus where every care was taken to exclude moisture, and the two middle fractions were collected. The miscibility temperatures of these were determined and the results are in Table II. Fraction I, Table I, was fractionally distilled through the ten-foot column, with the results shown in Table III. It would appear that distillation through an efficient column gives a drier alcohol than the use of aluminium amalgam.

TABLE II.

Fraction.	Vol., c.c.	M.T.
Original	500	50.8°
First	200	48.22
Second	200	52.96

TABLE III.

Fraction.	Vol., c.c.	M.T.
Original	750	47.42°
First	40	46.55
Second	500	45.51
Third	100	45.52
Fourth	100	46.65

Fractions 1 and 2, Table II, were mixed, distilled through the column, and examined, with the results shown in Table IV. Again the distillation method is effective.

TABLE IV.

Fraction.	Vol., c.c.	M.T.
Original	400	50.0°
First	30	46.2
Second	100	45.72
Third	250	45.64

TABLE V.

Fraction.	Vol., c.c.	M.T.
Original	620	47.02°
First	20	46.85
Second	200	45.52
Third	50	45.56
Fourth	200	45.60

It has been shown by several workers (*e.g.*, Noyes, *J. Amer. Chem. Soc.*, 1923, 43, 857) that freshly burnt lime removes water very effectively from alcohol, although it is a wasteful process. A fairly dry specimen of our alcohol, that had been freed from other impurities, was treated with lime. The alcohol was siphoned off from the lime and distilled through the column. The miscibility temperature results are in Table V. It will be noticed that 73% of the total distillate gives a miscibility temperature of approximately 45.5°. This was the value given by the one distillation alone through the column (see Table III, Fractions 2 and 3) and for 80% of the original material. Certainly, therefore, distillation alone produces quite as

dry a product as the lime treatment followed by distillation, and the large loss of alcohol is avoided. In view of the known efficacy of the lime treatment, the result indicated that acetone-free, dry methyl alcohol gave a miscibility temperature with *cyclohexane*, when the concentration of the latter was 69.15% by weight, of 45.52°.

A number of fractions of almost dry alcohol were mixed and twice redistilled through the column, every possible precaution being used to avoid the incursion of moisture. Table VI shows the miscibility temperature corresponding to the fractions collected in the second distillation. The results show that the alcohol is almost entirely water-free. The main fractions were siphoned over into a storage flask and used in the subsequent miscibility work. From time to time, redeterminations of the miscibility temperature were made to ensure that no moisture had entered the alcohol. The b. p. was 64.70°/760 mm., as determined in the apparatus described by Jones and Betts (J., 1928, 1177).

TABLE VI.

Fraction	Original	1	2	3	4	5	6
Vol., c.c.	2000	80	400	500	500	400	80
M.T.	45.62°	45.56°	45.53°	45.52°	45.53°	45.54°	45.66°

*cycloHexane*. This was from three sources: (a) *cyclohexane* "pur," Poulenc Frères, (b) *cyclohexane* "pure," Hopkin and Williams, and (c) synthetic material obtained by the catalytic method. The first two specimens had m. p. 2.6° and 1.0° respectively. Sabatier and Senderens give m. p. 6.5° for the pure material, whilst we have observed 6.48° both from the two purified commercial samples, and from the synthetic material obtained by us. Fractional freezing did not raise this m. p.

The *cyclohexane* melting at 2.6° was subjected to the usual process of purification by fuming sulphuric acid, but after two repetitions of the process the m. p. of the product still remained low, 4.2°. Moreover, there was considerable loss of material. The *cyclohexane* failed to decolorise potassium permanganate, and the impurity could not be removed by nitration. Fortunately, although distillation through a 12-bulb pear still-head produced no improvement, distillation through the ten-foot column, previously mentioned, gave good results, as the following record shows, 50% of the material being obtained pure in one distillation:

Fraction.	Vol., c.c.	M. p.	Fraction.	Vol., c.c.	M. p.
Original	430	2.6°	Fifth	40	5.8°
First	20	— 5.0	Sixth	50	6.1
Second	20	3.2	Seventh	30	6.3
Third	20	4.4	Eighth	200	6.48
Fourth	30	5.0	Residue	10	— 6.0

A similar difficulty was experienced with the second commercial sample (m. p.  $1^{\circ}$ ). Very slight purification resulted on continued sulphonation, but on distillation through the column, 50% of the original quantity was obtained with m. p. above  $6.0^{\circ}$ , and there was no difficulty in getting a pure specimen from this.

*Acetone.* A.R. Acetone (B.D.H.) was purified as described by Reilly and Ralph (*Sci. Proc. Roy. Dublin Soc.*, 1919, **15**, 597), and distilled twice through a twelve-pear column. It had b. p.  $56.35^{\circ}/760$  mm.

*Benzene.* Kahlbaum's benzene (for analysis) was fractionally crystallised several times, and a fraction of m. p.  $5.45^{\circ}$  was used throughout the work.

*Determination of the Solubility Curves.*—The synthetic method of determining the solubility curves has been described by Jones and Betts (J., 1928, 1177). Owing to the hygroscopic nature of the alcohol, simple but quite effective precautions were taken to avoid contact with atmospheric moisture. The containers of the alcohol and *cyclohexane* were fixed in desiccators containing phosphoric oxide. The lid of each desiccator had a ground-in vacuum stopper to which was firmly attached the stopper of the container, so that the two vessels were opened simultaneously. Small pipettes, themselves carefully protected against moisture, could be inserted into the liquid which yet remained in contact with the dry atmosphere. The lower stopper was of cork covered with tinfoil. The liquid was transferred to the experimental tubes, which were made of Pyrex glass and had been thoroughly dried by heating in the blowpipe and then kept in a desiccator. The filling of the tubes was effected inside a small box, 12" long,  $5\frac{1}{2}$ " wide, and  $5\frac{1}{2}$ " deep, with a glass front and back, and containing a vessel filled with calcium chloride. In the top of the box was a small hole which allowed a pipette to be inserted, and directly below this was a larger hole fitted with a cork, in which the weighed experimental tubes could be placed. Air, dried by calcium chloride and phosphoric oxide, was blown through the box during the filling. The *cyclohexane* was first run into the tube, the tube reweighed, reinserted in the cork, and the alcohol run in, forming the bottom layer. The tube was quickly taken out, sealed off, allowed to cool, and reweighed. That this simple procedure was sufficient to prevent any incursion of moisture was proved by the constancy of the miscibility temperature of dry methyl alcohol throughout several months. In the case of the systems methyl alcohol-acetone-*cyclohexane* and methyl alcohol-benzene-*cyclohexane*, solutions were made up in double stoppered bottles, the fillings being carried out as described above.

The thermometers used had been standardised recently at the N.P.L.

*Solubility Curve: Methyl Alcohol-cycloHexane.*—The miscibility temperatures,  $t^\circ$ , corresponding to various proportions (% by weight) are given in Table VII, and shown graphically in Fig. 1, Curve F. The critical phenomena are exceedingly clear, persistent emulsions are formed on shaking, and the intense blue colour

FIG. 1.

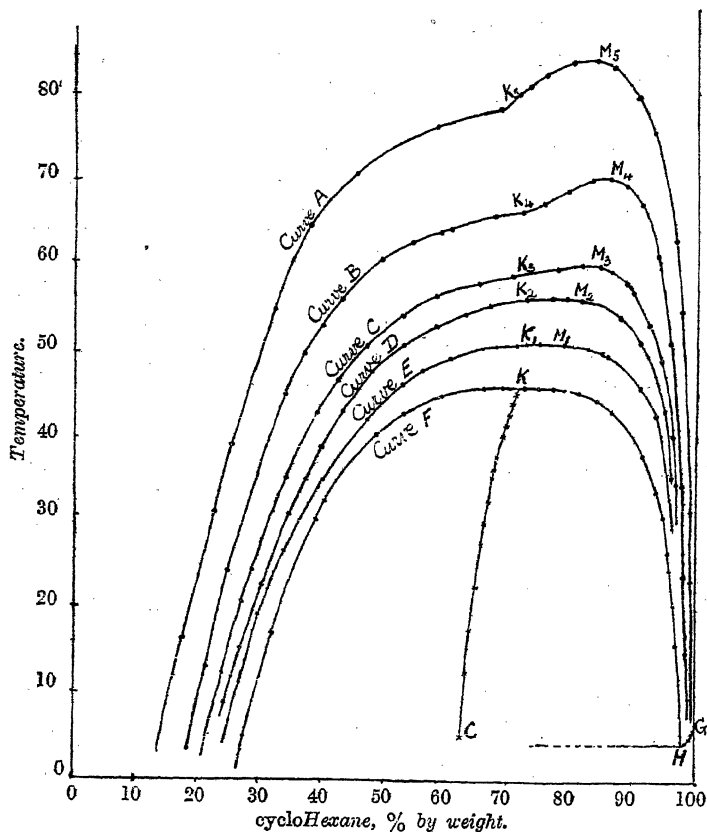


TABLE VII.

$C_6H_{12}$ , %.	$t$ .	$C_6H_{12}$ , %.	$t$ .	$C_6H_{12}$ , %.	$t$ .	$C_6H_{12}$ , %.	$t$ .
32-23	17.1°	66-18	45.45°	72.81	†45.58°	86.93	42.80°
39-40	30.4	69-15	45.52	77-60	45.53	91.47	37.5
48-96	40.05	69-86	45.56	79.26	45.45	93.40	32.3
53-60	42.68	70-80	*45.58	80.64	45.32	95.50	30.6
59-49	44.62	72-00	†45.60	81.25	45.10	97.30	6.1

\* Lower layer greater.

† Critical solution point; volumes of layers equal.

‡ Upper layer greater.

observable when the solution is examined in reflected light persists for several degrees above the *C.S.T.*

*The Effect of Water on the Solubility Curve.*—Solutions of methyl alcohol-water were made up in the dry box, and the determinations were carried out as usual. The results are in Table VIII and are shown graphically in Fig. 1, Curves E, D, C, B, A. The critical phenomena were slightly diminished in the presence of a trace of water, but with larger amounts they were more intense in the region of the ternary critical point; this was not the maximum point on these curves. Significant points are annotated as follows :

1 = Lower layer greater.  
2 = Volumes equal.

3 = Upper layer greater  
4 = Maximum point.

TABLE VIII.

$C_6H_{12}$ , %.	<i>t.</i>	$C_6H_{12}$ , %.	<i>t.</i>	$C_6H_{12}$ , %.	<i>t.</i>	$C_6H_{12}$ , %.	<i>t.</i>
0.331% Water in the alcohol.							
29.00	17.50°	47.16	42.08°	71.11	50.31°	84.90	49.51°
30.05	19.30	51.98	45.30	73.11	50.52	85.49	49.20
31.57	21.80	52.83	46.10	75.09	50.53(4)	90.80	45.35
34.10	26.75	55.84	47.78	78.90	50.40	93.50	42.09
39.60	34.35	65.70	50.10	80.10	50.35	95.60	36.20
40.10	35.06	66.73	50.26(1)	82.50	49.80		
0.800% Water in the alcohol.							
22.28	3.5°	56.15	51.57°	77.98	55.58°	92.07	49.55°
30.45	22.95	62.84	54.11(1)	85.90	54.64	95.49	42.8
43.82	43.20	71.25	55.64(3)	90.58	50.96	96.00	35.0
44.95	44.45	72.97	55.81(4)	91.79	50.10	97.57	25.5
53.09	50.61						
1.114% Water in the alcohol.							
24.30	12.5°	58.90	56.16°	81.84		59.43° (4)	
27.29	20.8	65.16	57.35 (1)	86.68		58.75	
29.17	24.35	70.76	58.23 (2)	89.82		56.47	
39.50	42.72	74.92	58.75	97.19		36.20	
47.17	50.20	78.04	59.04				
2.031% Water in the alcohol.							
21.83	13.05°	67.66	65.35° (1)	91.41		66.72°	
29.77	34.72	72.30	65.61 (3)	92.09		63.95	
37.78	49.62	79.84	68.24	95.66		50.83	
49.80	60.50	83.55	69.16	97.70		34.0	
59.10	63.38	86.32	69.42 (4)				
3.900% Water in the alcohol.							
17.78	16.5°	45.55	70.50°	72.79	80.30°	93.45	75.03°
22.41	31.30	52.95	73.67	75.80	81.75	93.68	74.39
24.40	36.42	58.35	75.76	80.20	83.15	94.83	73.10
25.52	39.20	65.84	77.65 (1)	83.40	83.16 (4)	94.43	59.25
32.50	54.98	69.18	77.75 (2)	86.25	82.75	99.22	16.6
38.00	64.87	71.14	79.25	89.45	80.60		

The ternary critical solution points,  $K_1$  to  $K_5$ , Fig. 1, and the corresponding maximal points,  $M_1$  to  $M_5$ , show increasing divergence as the concentration of water is increased. It is clear from the

figure that, by choosing a concentration of *cyclohexane* greater than the critical concentration, a greater rise in miscibility temperature would be obtained for a given percentage of water present in the alcohol. But it is necessary to preserve the accuracy of the reading itself, therefore 75% by weight of *cyclohexane* has been chosen as the optimum concentration, and pipettes were calibrated to give these proportions by weight in the system *cyclohexane*-anhydrous methyl alcohol. Our pipettes, which were constructed as described by Orton and Jones (J., 1919, 115, 1065), had the following volumes at 15°: for *cyclohexane*, 0.7570 c.c.; for anhydrous and aqueous methyl alcohol, 0.2485 c.c. We have confirmed in this work the great accuracy which can be obtained with this kind of pipette. A further improvement was made by grinding the tip, and bending the capillary at right angles about 4 mm. from the end. Table IX gives the miscibility temperatures which are obtained by using the relative volumes of liquids given above. The results when plotted indicate that the method becomes more sensitive as the percentage of water in the alcohol decreases. It is possible to estimate water within  $\pm 0.002\%$  if the miscibility temperature is read to  $0.02^\circ$ , a degree of accuracy which is readily obtainable with a little practice. An estimation within  $\pm 0.01\%$  could be made with ease.

TABLE IX.

Water content of alcohol, % ...	0.0	0.331	0.800	1.114	2.031	3.900
M.T. ....	45.55°	50.52°	55.74°	58.75°	66.50°	81.56°

The pipette volumes could be varied to give a percentage of *cyclohexane* within the limits 73—75% without appreciably affecting either the sensitiveness of the experimental reading or the quantitative figures given in Table IX, so long as the percentage of water in the alcohol was not greater than 1%.

A similar method may be developed in the case of ethyl alcohol, since this forms a *C.S.T.* with *cyclohexane* at (very roughly)  $-15^\circ$ , and preliminary experiments show that traces of water affect the binary *C.S.T.* to a large extent.

*Effect of Benzene and Acetone on the System Methyl Alcohol-cycloHexane.*—Solutions of benzene in *cyclohexane* and of acetone in methyl alcohol were prepared, and used for the determination of the miscibility temperatures.

*Benzene in cyclohexane.* The miscibility results obtained when 10.19% of benzene is present in the *cyclohexane* are in Table X. It was found that the *C.S.T.* was lowered by approximately  $12.3^\circ$ , i.e., 1% of benzene lowers the *C.S.T.* by  $1.21^\circ$ . A noteworthy point was that the critical phenomena which were so marked in the system methyl alcohol-*cyclohexane* were almost entirely absent at

the ternary critical point, but nevertheless the saturation points were very sharp and easily read to  $0.02^\circ$ . At the ternary critical point the percentage by weight of methyl alcohol was less than at the maximum saturation point.

TABLE X.

$C_6H_{12} + C_6H_6$ mixture,								
% (by wt.)	33.81	38.50	45.99	47.99	58.27	58.84	61.60	64.36
M.T. ....	$11.6^\circ$	$18.05^\circ$	$26.55^\circ$	$27.92^\circ$	$32.96^\circ$	$33.02^\circ$	$33.32^\circ$	$*33.50^\circ$
$C_6H_{12} + C_6H_6$ mixture,								
% (by wt.)	69.25	71.47	76.51	80.37	83.10	86.34	90.45	95.00
M.T. ....	$33.35^\circ$	$\dagger 32.85^\circ$	$32.43^\circ$	$31.42^\circ$	$30.87^\circ$	$29.50^\circ$	$26.70^\circ$	$18.1^\circ$

\* Critical point—volumes equal.

† Maximum saturation point.

*Acetone in methyl alcohol.* In Table XI are given similar results obtained when 9.18% of acetone is present in the methyl alcohol. The *C.S.T.* was lowered by  $6.15^\circ$ , i.e., 1% of acetone lowers the *C.S.T.* by  $0.67^\circ$ . The mixture at the maximum saturation point contained a greater percentage of *cyclohexane* than that at the ternary critical point. The critical phenomena were more pronounced than in the binary system.

TABLE XI.

$C_6H_{12}$ , % .....	27.50	33.86	42.60	46.74	54.61	62.51	69.62
M.T. ....	$7.5^\circ$	$17.4^\circ$	$28.75^\circ$	$33.10^\circ$	$36.35^\circ$	$38.45^\circ$	$*39.45^\circ$
$C_6H_{12}$ , % .....	75.79	79.38	82.83	84.15	89.80	94.33	98.60
M.T. ....	$\dagger 40.15^\circ$	$40.12^\circ$	$39.85^\circ$	$39.42^\circ$	$37.25^\circ$	$34.60^\circ$	$25.0^\circ$

\* Critical point—volumes equal.

† Maximum saturation point.

The sensitiveness of the miscibility temperature to such impurities as acetone in the alcohol or benzene in the *cyclohexane* is of advantage when the purpose is to estimate the percentage of water present. Moreover, their effects on the miscibility temperature are but slightly altered by the presence of up to 0.5% of water in the alcohol.

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## CLXX.—The System *cyclohexanol* and Water.

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WORK on this system had previously been done by de Forcrand, who, after obtaining *cyclohexanol* in a purer condition than previous workers had done, measured several of its physical properties, including the freezing point and mutual solubility with water at  $11^\circ$  (*Compt. rend.*, 1912, 154, 1327, 1767); he then investigated the

binary system of the alcohol and water over a range of concentrations of *cyclohexanol* from 89.86 to 100% by weight, and concluded from his results that a compound  $C_6H_{12}O, \frac{1}{2}H_2O$  existed (*ibid.*, 1912, 155, 118).

The present work is an investigation of the greater part of the system, the range of concentration of *cyclohexanol* being 0—93% by weight, which is sufficient to include the two-liquid-phase region and most of the ice line.

#### EXPERIMENTAL.

*Purification of cycloHexanol.*—The *cyclohexanol* was obtained from British Drug Houses, Ltd., and purified by fractional distillations at a pressure of about 10 mm. of mercury, the head and tail fractions being rejected. Schreiner and Frivold (*Z. physikal. Chem.*, 1926, 124, 1) claim to have obtained a product melting at 23.3—23.9° (de Forcrand gives 22.45°) by two fractionations at 2—3 mm., but in the present case no fraction melting higher than 20.6° could be obtained from successive fractionations (the m. p.'s being taken in the first receiver of the distillation apparatus itself). A solution of this *cyclohexanol* in water gave no trace of a precipitate with bromine water, nor did it immediately destroy the bromine colour, indicating that no appreciable amount of phenol was present and that the most probable remaining impurity was water. Since the cryoscopic constant of *cyclohexanol* is so large (382.8 according to de Forcrand), the m. p. of our specimen would correspond to a purity of 99.85% by weight, if 23.6° is taken as the true melting point; hence, as water was to be the other component and its concentration was not to be less than 7%, further purification was deemed unnecessary.

Owing to the extremely hygroscopic nature of the alcohol, stock solutions containing about 95% of it were used, as these were not at all hygroscopic.

*Measurement of Points in the Binary System.*—The points on the liquid-liquid curve were obtained by the usual synthetic method, sealed glass bulbs being used at the higher temperatures. When the proportion of *cyclohexanol* was large, the temperature at which turbidity appeared increased with successive heatings, and, as this was presumably due to decomposition, the first reading was taken in such cases. It was found impossible to obtain points on this curve from 87.9% onwards, for, owing to the steepness of the curve after this point, the turbidity was extremely faint and no accurate determination of the temperature at which it occurred could be made.

The solid separation points over the range 88—93% of *cyclohexanol* were difficult to obtain, since considerable supercooling



was necessary before a solid would separate, and when this eventually occurred the temperature did not rise appreciably. However, by supercooling to produce the solid and then allowing the mixture to warm slowly, and noting at what temperature a trace of the solid could just be retained, approximate values (accurate probably to within  $0.5^\circ$ ) were obtained. This difficulty did not arise in tracing the ice line from 0 to 5% of *cyclohexanol*, for here, when supercooling ceased, there was the usual quick rise to a steady temperature.

The results obtained are given in the following tables and are plotted, together with those of de Forcrand, in Fig. 1.

(1) *The Ice Line.*

<i>cyclohexanol</i> , % by wt.	M. p.	<i>cyclohexanol</i> , % by wt.	M. p.	<i>cyclohexanol</i> , % by wt.	M. p.
1.67	$-0.3^\circ, 0.32$	88.3	$-1.2^\circ$	90.45	$-4.9^\circ$
3.33	$-0.6$	88.45	$-1.1$	91.2	$-7.6$
5.00	$-0.9$	89.0	$-2.0$	92.3	$-10.2$
		90.08	$-4.1$	93.0	$-15.4$

(2) *The Liquid-Liquid Curve.*

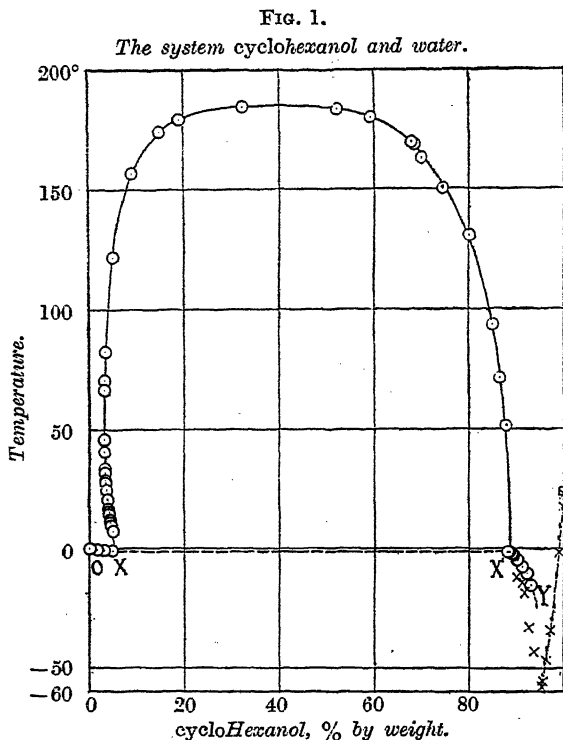
<i>cyclohexanol</i> , % by wt.	Turbidity temp.	<i>cyclohexanol</i> , % by wt.	Turbidity temp.	<i>cyclohexanol</i> , % by wt.	Turbidity temp.
3.18	$40.45^\circ$ & $70.45^\circ$	4.29	$15.2^\circ$	52.3	$183.66^\circ$
3.19	$45.8$ & $66.3$	4.41	$11.2$	59.4	$180.1$
3.26	$40.4$	4.55	$12.0$	68.0	$169.7$
3.37	$31.85$ & $82.4$	4.58	$9.7$	68.5	$168.64$
3.41	$33.6$	4.78	$9.4$	70.1	$163.03$
3.52	$27.55$	5.00	$7.2$	74.6	$150.35$
3.57	$28.7$	5.14	$121.95$	80.2	$130.9$
3.75	$24.6$	9.22	$156.9$	85.3	$93.63$
3.82	$20.8$	15.00	$174.3$	85.95	$72.75$
3.95	$20.6$	19.2	$179.4$	86.75	$71.5$
4.09	$16.3$	32.4	$184.72$	87.9	$51.55$
4.23	$14.2$				

*Discussion of Results.*

The liquid-liquid system has been examined for water and the following alcohols: *n*-butyl (Orton and Jones, J., 1919, **115**, 1194), *isobutyl* (Alexejew, *Wied. Ann.*, 1886, **28**, 305), *sec*-butyl (*idem*, *ibid.*; Dolgolenko, *Z. physikal. Chem.*, 1908, **62**, 499; Timmermanns, Thèse, Bruxelles, 1911), and *isoamyl* (Fontein, *Z. physikal. Chem.*, 1910, **73**, 212). All these resemble *cyclohexanol* in showing reversed solubility curves on the water side, and all except *sec*-butyl alcohol in not showing this on the alcohol side.

The existence of the solid hydrate described by de Forcrand (*loc. cit.*) was not confirmed. His solid curve resembles ours but is at a lower temperature, probably because supercooling was not sufficiently avoided. The rapid decrease of steepness of the slope of the curve YX' as the two-liquid-phase region is approached is a consequence of the flattening out of the vapour pressure-concen-

tration curve prior to becoming a straight line parallel to the concentration axis in this region itself (Sidgwick and Turner, J., 1922, 121, 2262). There is no sign of a maximum at the concentration corresponding to the composition  $C_6H_{12}O, \frac{1}{2}H_2O$  (91.74% *cyclohexanol*) or of a sharp discontinuity after it; moreover, since a mixture whose total composition lies between X and X' can be in equilibrium with



Present research—○—. Schreiner and Frivold—□—. de Forcrand—×—

only one solid phase, the solid separating out along either OX or X'Y must be the same substance and, since there is no eutectic in OX, this substance must be ice. Its appearance agreed with that given by de Forcrand, viz., "small opaque crystals." The occurrence of some combination in solution between the alcohol and the water may, however, be assumed to be probable from the existence of the reverse solubility curve.

Our thanks are due to Imperial Chemical Industries, Ltd., for a grant towards the cost of this work.

THE DYSON PEREINS LABORATORY,  
OXFORD.

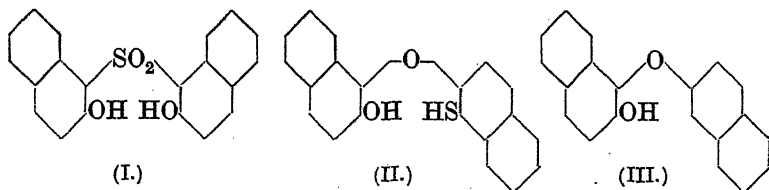
[Received, April 29th, 1930.]

CLXXI.—*Dehydro-2-naphtholsulphone.*

By LEONARD ARTHUR WARREN and SAMUEL SMILES.

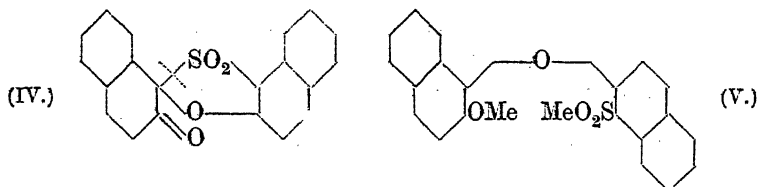
HINSBERG has shown (*J. pr. Chem.*, 1914, **90**, 345; 1915, **91**, 307; 1916, **93**, 277) that alkaline ferricyanide removes two hydrogen atoms from 2-naphtholsulphone (I), forming the dehydro-sulphone, and that the latter substance by alkaline reduction yields *iso*-2-naphtholsulphone, two hydrogen atoms being reabsorbed in the process. He regarded these isomerides as having identical structures and as providing a further illustration of the valency isomerism advocated by him to explain the relations between 2-naphthol 1-sulphide and *iso*-2-naphthol sulphide. The last-named substance has been shown (this vol., p. 956) to be the 2-hydroxy-1'-thiol derivative (II) of 1:2'-dinaphthyl ether; moreover it evidently is closely related to the *iso*-sulphone, since Hinsberg (*loc. cit.*) has shown that it is formed from an anhydride of this by reduction.

It is thus evident that the structures of *iso*-2-naphtholsulphone and of the dehydro-sulphone need reconsideration; experiments have now been made further to elucidate the nature of these derivatives of 2-naphtholsulphone and their relationship to the corresponding derivatives of 2-naphthol 1-sulphide (I, SO<sub>2</sub> being replaced by S). Of the many important facts bearing on these issues recorded by Hinsberg (*loc. cit.*), it is sufficient to mention the isolation of 2-hydroxy-1:2'-dinaphthyl ether (III) from the reduction products of the dehydro-sulphone and the spontaneous formation of this ether and sulphur dioxide from the *iso*-sulphone. These facts appear to indicate the presence in these substances of the 1:2'-dinaphthyl ether structure which has been found (this vol., p. 956) in the dehydro- and the *iso*-sulphide. Hinsberg, indeed, discussed the question whether the *iso*-sulphone should be regarded as the sulphinic acid derived from this ether, but rejected the suggestion for the following reasons: (a) both 2-naphthol-1-sulphone (I) and the *iso*-sulphone yield the dehydro-sulphone by oxidation, (b) the



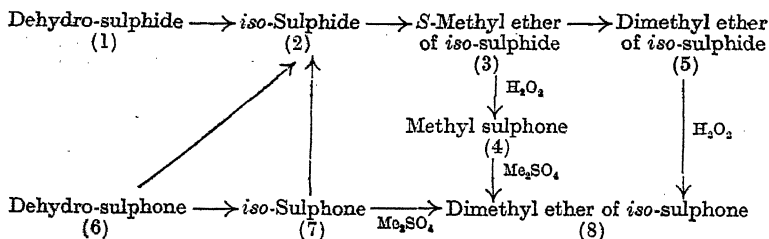
*iso*-sulphide by methylation and oxidation gives the dimethyl ether of the *iso*-sulphone, (c) the *iso*-sulphone can be converted into the *iso*-sulphide by reduction of a substance regarded as its anhydride,

Since the *iso*-sulphide is now known to be (II), the relations (b) and (c), if confirmed, entirely lose their effectiveness in refuting the 1:2'-oxide structure; on the contrary, they now appear strongly to support this structure for the *iso*-sulphone. The first of the three relations quoted has clearly little value unless the dehydro-sulphone is known or assumed not to contain the 1:2'-oxide structure. Important evidence on this question is afforded by reduction of the dehydro-sulphone; with sodium amalgam or with zinc and acetic acid (also Hinsberg, *loc. cit.*) the 2-hydroxy-1:2'-dinaphthyl ether (III) is formed, whilst with zinc and hydrochloric acid the *iso*-sulphide (II) is obtained. The dehydro-sulphone therefore contains the 1:2'-oxide structure and, since it is formed merely by removal of two hydrogen atoms from 2-naphthol-1-sulphone (I), the structure (IV) must be ascribed to it. As was shown by Hinsberg (*loc. cit.*), the dehydro-sulphone reacts slowly with *p*-nitrophenyl-



hydrazine, fission of the substance occurring with formation of the hydrazone of  $\beta$ -naphthaquinone. This behaviour is analogous to that of dehydro-1-bromo-2-naphthol with aniline (Pummerer and Cherbuliez, *Ber.*, 1919, 52, 1412), which yields the anilino-derivative of  $\beta$ -naphthaquinone.

The chief relations between the members of this group are summarised as follows; the substances are numbered to facilitate reference.



Previous experiments have shown (this vol., p. 956) that (1), (2), (3), and (4) yield the hydroxydinaphthyl ether (III) with suitable reducing agents; it is now shown that (6) and (7) also yield this substance with sodium amalgam, and (8) gives the methyl ether (III, OH being replaced by OMe). The 1:2'-dinaphthyl ether

structure has in fact been established for all these with the exception of (5). The important relationships of (3), (4), and (5) to (8) indicated by Hinsberg (*loc. cit.*) have been confirmed, but the substance, m. p.  $88^{\circ}$ , described by him as the dimethyl ether of the *iso*-sulphone (8) has not been encountered. Moreover the conversion of (6) and (7) into the *iso*-sulphide (II) has been effected by suitable reduction.

The nature of the *iso*-sulphone is clearly revealed by the formation of the mercaptan (II) from it by reduction and by the fact that its *dimethyl* ether has the structure (V), which is assigned to it because reduction yields the methoxydinaphthyl ether (III, OH being replaced by OMe) and the substance is formed by methylation of the methyl sulphone (II, SH being replaced by  $\text{SO}_2\text{Me}$ ) (this vol., p. 956) or by oxidation of the dimethyl ether of the *iso*-sulphide (II, OH and SH being replaced by OMe and SMe respectively). Hence the *iso*-sulphone itself is to be regarded as the sulphinic acid corresponding to the thiol (II, SH being replaced by  $\text{SO}_2\text{H}$ ), and its formation from the dehydro-sulphone (IV) by reduction as taking place by rupture of the 5-membered ring as indicated, the process being analogous to the formation of the *iso*-sulphide (II) from the dehydro-sulphide (IV,  $\text{SO}_2$  being replaced by S) (this vol., p. 956). Moreover, conversion of the *iso*-sulphone and 2-naphthol-1-sulphone into the dehydro-sulphone is thus seen to proceed similarly to the oxidation of *iso*-2-naphthol sulphide and 2-naphthol 1-sulphide to the dehydro-sulphide.

#### EXPERIMENTAL.

*Dehydro-2-naphthol-1-sulphone* (IV).—Details of the preparation of this substance were not described by Hinsberg. The following method gave the best results. An aqueous solution (150 c.c.) of potassium ferricyanide (10 g.) was gradually added to a shaken mixture of chloroform (100 c.c.) and water (125 c.c.) which contained 2-naphthol-1-sulphone (5 g.) and sodium hydroxide (1.2 g.). After further agitation (1 hour) the chloroform solution was dried and concentrated. The dehydro-sulphone separated (yield, *ca.* 50%) in the crystalline state and after purification from acetic acid formed bright yellow prisms, m. p.  $245^{\circ}$  (Found : C, 68.9; H, 3.7. Calc. : C, 68.9; H, 3.4%).

*The Dimethyl Ether of the iso-Sulphone* (V).—The *iso*-sulphone was obtained from the dehydro-sulphone by reduction with sodium sulphide as described by Hinsberg. The chief properties attributed by him to the substance and its solubility in aqueous sodium carbonate were confirmed. A solution of this material in excess of aqueous sodium hydroxide (2*N*) was treated in the usual way with

methyl sulphate. The viscous product was further treated with boiling 1% alkali solution. It solidified when cooled and was obtained from acetone-methyl alcohol (charcoal) in prisms, m. p. 144° (Found: C, 69.8; H, 4.9; *M*, 385.  $C_{22}H_{18}O_4S$  requires C, 69.8; H, 4.7%; *M*, 378).

The same substance was obtained by the following methods: (a) A suspension of the sodium salt of the methyl sulphone (II, SH being replaced by  $SO_2Me$ ) derived (this vol., p. 956) from the *iso*-sulphide was treated in warm aqueous sodium hydroxide with methyl sulphate as usual. The semi-solid product was purified by the treatment already described; it then had the same m. p. as the product prepared from the *iso*-sulphone, whether taken alone or mixed with it. (b) A solution of the viscous dimethyl ether of the *iso*-sulphide (II, OH and SH being replaced by OMe and SMe respectively) (1.7 g.) in acetic acid (15 c.c.) containing hydrogen peroxide (2 c.c., 30% sol.) was warmed (1 hour, 100°). When sodium chloride was added to the cooled and diluted liquid, the desired product separated in the crystalline state; this was purified from acetic acid and identified in the usual manner with the products from the two other methods described.

*iso*-2-Naphthol Sulphide (II).—(a) Dehydro-2-naphtholsulphone (IV; 1 g.) was suspended in boiling acetic acid (40 c.c.) containing concentrated hydrochloric acid (5 c.c.). Zinc dust was gradually added until the colour of the solution was discharged. The clear solution was mixed with a little concentrated hydrochloric acid, cooled, and stirred, and water (20 c.c.) slowly added. The crystalline precipitate obtained, after further purification (77% yield), was identified with an authentic sample of *iso*-naphthol sulphide (Found: C, 75.5; H, 4.4. Calc.: C, 75.5; H, 4.4%). This *iso*-sulphide responds to Rheinboldt's test (*Ber.*, 1927, 60, 184) for aromatic thiols.

(b) Reduction of *iso*-2-naphtholsulphone (II, SH being replaced by  $SO_2H$ ) was effected by zinc and concentrated hydrochloric acid in boiling alcohol. Addition of water to the cooled liquid gave a crystalline precipitate. This was purified from alcohol and found to be identical with an authentic sample of *iso*- $\beta$ -naphthol sulphide.

2-Hydroxy-1:2'-dinaphthyl Ether (III).—(a) Zinc dust was added to a hot solution of the dehydro-sulphone (IV; 1 g.) in acetic acid (30 c.c.) until the colour had faded. The cooled solution deposited the hydroxydinaphthyl ether (90% yield), m. p. 197° (Found: C, 83.6; H, 5.2. Calc.: C, 83.9; H, 4.9%), which was further identified by a close comparison of its methyl ether with synthetic material (this vol., p. 956). Reduction of the dehydro-sulphone with sodium amalgam in warm aqueous alcohol gave a poorer yield

of the same material. It was isolated from the product of reaction by addition of sulphuric acid after alcohol had been removed by evaporation (charcoal); it was purified from acetic acid and had m. p. 197°.

(b) The *iso*-sulphone (II, SH being replaced by SO<sub>2</sub>H) also yielded the hydroxydinaphthyl ether by reduction with these reagents. Reduction with zinc and acetic acid was effected as described in the case of the dehydro-sulphone; the yield was poorer. A solution of the *iso*-sulphone (from 1 g. of dehydro-sulphone) in *N*-sodium hydroxide was stirred and treated with sodium amalgam (35 g.; 5%) for 3 hours. The clear aqueous liquid (charcoal) was rendered acid and set aside. The required substance separated and was purified (m. p. 197°) and identified in the usual manner.

2-Methoxy-1:2'-dinaphthyl ether (III, OH being replaced by OMe) was obtained by alkaline methylation of the product of reduction of the dehydro-sulphone with zinc and acetic acid. It was purified from acetic acid and had m. p. 161° (Found: C, 84.0; H, 5.7. Calc.: C, 84.0; H, 5.3%) and was identical with the product obtained by synthesis (this vol., p. 956). The same substance was obtained by reduction of the dimethyl ether of the *iso*-sulphone (V). Sodium amalgam (5%) was gradually added (6 hours) to alcohol (40 c.c.) and water (20 c.c.) which contained this ether in suspension. The alkaline liquid was mixed with acetic acid and boiled (charcoal). When diluted and cooled, the solution yielded the required substance (0.2 g.), which was purified in the usual manner; m. p. 161° (Found: C, 83.7; H, 5.4. Calc.: C, 84.0; H, 5.3%).

In conclusion we wish to thank Dr. A. Cohen for a quantity of the dehydronaphtholsulphone and for information concerning its preparation.

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[Received, April 8th, 1930.]

## CLXXII.—*The Solubilities of Nitrophenols in Aqueous Ethyl-alcoholic Solutions.*

By JAMES COOPER DUFF and EDWIN JOHN BILLS.

It was shown by one of us (Duff, J., 1929, 2789) that *p*-nitrophenol in aqueous methyl-alcoholic solutions at 25° and 40° had solubility curves in which critical points occurred where the solvent was composed of methyl alcohol and water in simple molecular proportion. The positions of the critical points varied with the tem-

perature. *o*-Nitrophenol gave no indication of an alcohol hydrate at 25°, and only one ( $3\text{CH}_4\text{O}\cdot\text{H}_2\text{O}$ ) was indicated at 40°.

The behaviour of *o*-, *m*-, and *p*-nitrophenols in aqueous ethyl-alcoholic solutions has now been examined. Solubilities for *m*-nitrophenol were determined at 0°, 12·5°, and 25°; and these three temperatures and also 40° were used for *p*-nitrophenol, since this isomeride yielded the most characteristic results. *o*-Nitrophenol was considered only at 25°, this being sufficient for comparison with the results obtained from the other two isomerides.

The solubilities of the three nitrophenols in water have been determined by Sidgwick, Spurrell, and Davies (J., 1915, 107, 1202); and those in absolute ethyl alcohol over a wide range of temperature by Carrick (*J. Physical Chem.*, 1921, 25, 628). His method, synthetic in character, differs from ours, but our results for absolute alcohol agree with his.

Solubilities are expressed as g. per 100 g. of solvent throughout.

#### EXPERIMENTAL.

Kahlbaum's ethyl alcohol of 99·8% purity was used. The nitrophenols were recrystallised by the usual methods before use. The solubilities were determined for *o*- and *p*-nitrophenols in the same way as for aqueous methyl-alcoholic solutions (Duff, *loc. cit.*). The results for *m*-nitrophenol were obtained by the same synthetic method as that previously used for *p*-nitrophenol.

*o*-Nitrophenol (Fig. 1).—The solubility was determined at 25° in aqueous-alcoholic solutions over the range 0—100% alcohol. The results are given below, and the resulting curve (AB) presents no unusual features. During solution at 25° the *o*-nitrophenol did not form any oily liquid phase.

EtOH, % ...	0	30	40	50	60	70	80	90	100
S .....	0·25	0·7	1·7	3·9	7·4	12·2	21·0	32·5	46·0

*m*-Nitrophenol (Fig. 1).—(a) *Solubilities at 0°*. No oily phase was formed. The solubility curve (CDEF) is a straight line between D and E, points which correspond approximately to 33% and 90% of alcohol in the solvent.

EtOH, %	0	20	30	40	50	60	70	80	90	100
S .....	0·9	1·6	5·0	19·8	36·8	53·7	71·5	89·5	106·6	115·5

(b) *Solubilities at 12·5°*. The results for the curve CKHM are given in Table I. In solvents ranging from 24 to 46% of ethyl alcohol, *m*-nitrophenol produces two liquid phases, and saturation with this phenol ended with two liquid phases in contact with the solid. Determinations of these end points gave the straight line GLH, the results for which are in Table II. Since GLH is a straight



line, the two saturated liquid phases are evidently the saturated aqueous solution for solvent containing 24% of alcohol and the oily saturated solution for solvent of 46% alcohol. The area GLHKG is the field in which two liquid phases co-exist.

FIG. 1.

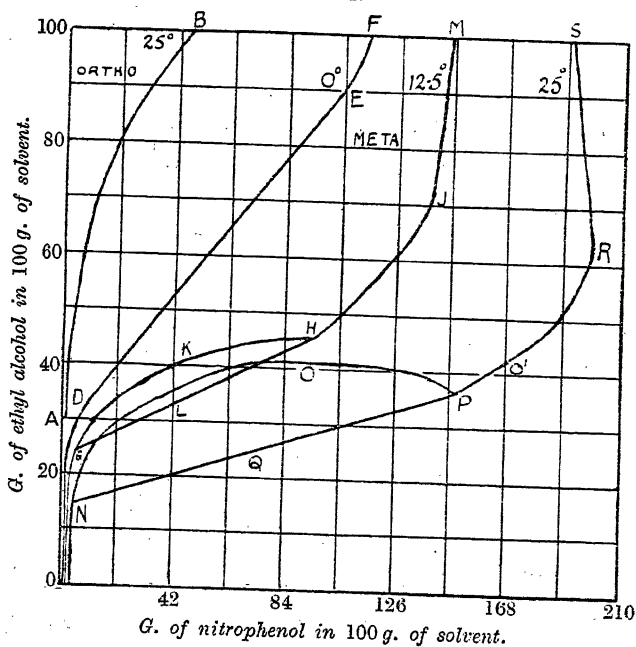


TABLE I.

EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.
0	1.2	35	27.2	46	96.0	70	139.5
20	2.5	40	41.0	50	106.2	80	143.5
25	6.8	42	52.1	60	126.2	90	146.0
27.5	8.9	45	74.4	63	131.0	100	148.0
30	12.8						

TABLE II.\*

EtOH, %	25	27.5	30	35	40	42	45
S	10.3	17.9	30.5	51.0	71.5	80.5	92

\* Two liquid phases remain at end-point.

(c) *Solubilities at 25°.* The results for the curves CNO and O'RS are given in Table III. In solvents ranging from 15 to 42% of ethyl alcohol, *m*-nitrophenol produces two liquid phases, which co-exist in the area NOPQN. The results yielding the lines NP and PO are given as  $S_1$  in Table IV. Along the line PO the two liquid phases become one on addition of sufficient *m*-nitrophenol.

The minimum alcoholic content of solvent in which this occurs is 36% (P) and the maximum is 42% (O). By saturation of the solutions which gave PO, the values  $S_2$  (Table IV) and hence the curve PO' were obtained. Along the line NP are two saturated liquid phases which, since NP is a straight line, are composed of the saturated aqueous solution for 15% alcoholic and the saturated oily solution for 36% alcoholic solvent. At 25° *m*-nitrophenol was

TABLE III.

EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.
0	1.35	35	43.5	44	174.0	63	204.0
10	1.7	37.5	52.2	45	179.0	70	202.0
15	4.0	39	59.8	46	186.0	80	200.0
20	6.5	40	65.9	50	189.0	90	197.5
25	11.0	41	81.5	60	201.0	100	195.0
30	25.0	42	171.0				

TABLE IV.

EtOH, %	15	20	25	30	35	36	37.5	39	40	41
$S_1$ .....	5.9*	38.8*	76.5*	106.3*	147.0*	150†	142†	140†	135†	122.5†
$S_2$ .....	—	—	—	—	—	150	156	162	165	167

\* Two liquids remain at end-point.

† Two liquids became miscible at end-point.

more soluble in 63% alcohol (R) than in absolute alcohol, whereas at the lower temperatures no maximum occurred.

*p*-Nitrophenol (Fig. 2).—(a) *Solubilities at 0°*. The results are given in Tables V (curve ACG) and VI (straight line BED). The curve as a whole resembles that obtained for *m*-nitrophenol at 12.5°. The alcohol limits in the solvent for producing two liquid phases (co-existing in the area BCDEB) are 25% and 51%. Along the straight line BED two saturated liquids are in equilibrium with solid *p*-nitrophenol. These liquids are respectively aqueous saturated solution in 25% alcohol and oily saturated solution in 51% alcohol.

TABLE V.

EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.
0	0.5	35	12.5	51	82.0	70	120.0
10	0.6	40	25.0	54	96.0	80	118.0
25	1.4	45	41.0	56	101.0	90	117.0
30	5.2	50	58.5	60	108.0	100	116.4

TABLE VI.\*

EtOH, % .....	27.5	30	35	40	45	50
S .....	9.2	15.2	30.0	44.8	61.0	76.0

\* Two liquids remain at end-point.

(b) *Solubilities at 12.5°*. The results are given in Tables VII (curves AHJ and JMN) and VIII ( $S_1$ , straight line HLK and

curve KJ;  $S_2$ , curve KJ'). For solvents containing between 17.5 and 45% of alcohol, it is possible to have two liquid phases co-existing (area HJKLH); 41% is the minimum alcoholic content to enable two liquid phases to become miscible (K) by saturation with *p*-nitrophenol at 12.5°.

FIG. 2.

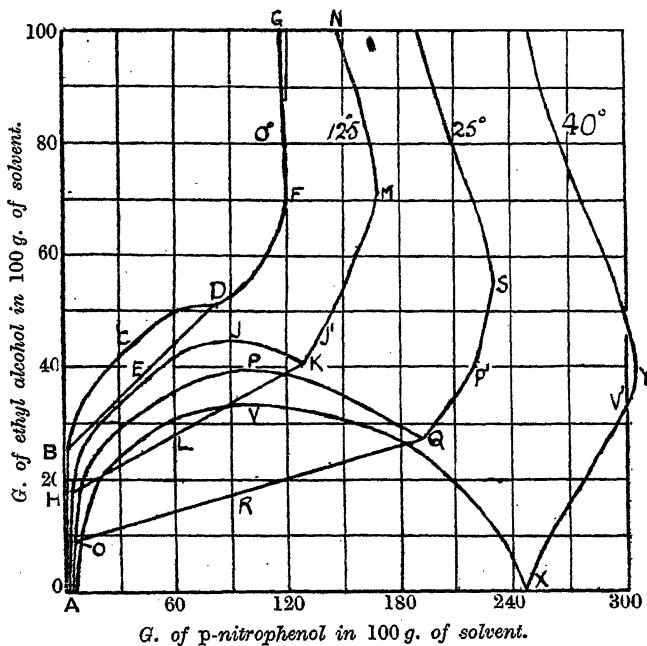


TABLE VII.

EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.
0	1.1	35	33.5	45	135.5	72	169.0
15	1.8	40	53.2	46	137.0	75	167.0
17.5	3.6	41	56.1	50	144.0	80	164.0
20	5.8	42	63.5	60	156.0	90	157.0
25	8.8	44	80.8	70	168.0	100	147.0
30	17.4						

TABLE VIII.

EtOH, %.	17.5	20	25	30	35	40	41	42	44	45
$S_1$ .....	4.0*	18.0*	41.0*	68.6*	92.5*	127.0*	127.8†	124.0†	108.8†	—
$S_2$ .....	—	—	—	—	—	—	127.8	130.3	133.0	135.5

\* Two liquids remain at end-point.

† Two liquids become miscible at end-point.

(c) *Solubilities at 25°*. The results are given in Tables IX (curves AOP and P'ST) and X ( $S_1$ , straight line ORQ and curve QP;  $S_2$ , curve QP'). For solvents containing between 8 and 39% of ethyl

alcohol, two liquid phases can co-exist (area OPQRO) and they can become miscible if the alcoholic content of the solvent is not less than 27% (point Q). Along the line ORQ exist two saturated solutions which are aqueous saturated solution in 8% alcohol and oily saturated solution in 27% alcohol.

TABLE IX.

EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.
0	1.6	25	19.2	38.5	80.5	60	227.0
10	3.4	27.5	26.2	39	220.0	70	220.0
15	5.2	30	34.9	40	220.5	80	208.9
17.5	6.0	32.5	45.7	46	223.0	90	199.0
20	8.5	35	57.8	50	226.1	100	189.5
22.5	13.7	37.5	70.1	56	230.4		

TABLE X.

EtOH, %...	9	10	12.5	15	17.5	20	22.5	25	26.5
$S_1$ .....	7.8*	17.5*	42.5*	65.6*	95.6*	118.7*	141.6*	169.1*	186.2*

\* Two liquids remain at end-point.

EtOH, %	27	27.5	30	32.5	35	37.5	38.5
$S_1$ .....	192†	191†	177.1†	160.5†	147.9†	132.7†	117.6†
$S_2$ .....	192	194	198	206.1	210.5	217.9	218.7

† Two liquids become miscible at end-point.

(d) *Solubilities at 40°.* At this temperature two liquid phases can co-exist (area AVXA) in solvents containing between 0 and 33.8% of ethyl alcohol. The two liquids can become miscible along the line XV on addition of sufficient *p*-nitrophenol. The results at 40° are given in Tables XI (curves AV and V'YZ) and XII ( $S_1$ , curve XV;  $S_2$ , curve XV').

TABLE XI.

EtOH, %.	S.	EtOH, %.	S.	EtOH, %.	S.
0	2.9	32.5	79.5	50	298
10	5.5	33.3	95.0	60	289
15	9.0	33.8	300.5	70	276
20	19.0	35	303.0	80	265
25	36.5	39	306.0	90	255
30	55.1	40	305.0	100	250.0

TABLE XII.

EtOH, % ...	0	10	15	20	25	30	32.5	33.3	33.8
$S_1$ .....	246*	233*	220*	206*	190*	149*	114*	101*	—
$S_2$ .....	246	258	268	277	286	296	299	—	300.5

\* Two liquids become miscible at end-point.

The above results show that in aqueous ethyl-alcoholic solutions *p*-nitrophenol has a maximum solubility at 0° and 12.5° in 72% alcohol, at 25° in 56% alcohol, and at 40° in 39% alcohol.

*Discussion of Results.*

The results obtained for the solubility of *o*-nitrophenol serve to emphasise the special features of the solubility curves of the *m*- and *p*-isomerides. The last two exhibit a marked tendency to form oily solutions at low temperatures, therein differing from *o*-nitrophenol, although this isomeride has a much lower m. p. ( $44^{\circ}$  as against  $116^{\circ}$  for *p*-nitrophenol) than the others. The greatest tendency to produce two liquids during solution in dilute alcoholic solutions is shown by *p*-nitrophenol: this is possibly connected with the greater ease with which this isomeride forms addition compounds with weak bases and with its own metallic derivatives; moreover, the salts of *p*-nitrophenol show the highest degree of hydration, whilst those of *o*-nitrophenol are, in general, the least hydrated. It seems probable, therefore, that the additive powers of *m*- and *p*-nitrophenol enable them to produce the oily liquid phases which characterise the looped portions of their solubility curves. The curves show that, as the temperature rises, there is a fall in the maximum alcohol concentration of the solvent determining the area in which two liquid phases co-exist.

Some of the curves show as many as four significant points; e.g., in the curve (Fig. 2) for *p*-nitrophenol at  $25^{\circ}$ , the point S shows maximum solubility, points P and O are the upper and lower limits, respectively, for the co-existence of two liquids, and point Q indicates the minimum alcohol concentration of solvent in which two liquid phases can be made completely miscible. The occurrence of maximum solubility for *m*- and *p*-nitrophenol at temperatures above  $12^{\circ}$  in aqueous ethyl-alcoholic solutions was unexpected, since this was not the case for methyl alcohol (Duff, *loc. cit.*). In considering the direction changes of the curves in Figs. 1 and 2, it is noteworthy that McCombie and his co-workers (J., 1921, 119, 970; 1922, 121, 243, 2308), studying the rates of saponification of esters by potassium hydroxide in aqueous ethyl-alcoholic solutions, found significant points in the resultant curves at which the alcohol and water in the solvent were present in simple molecular proportions. These points, however, were not all evident at any one temperature. Dexter, McCombie, and Scarborough (J., 1923, 123, 1229) studied an example of isomeric change in aqueous ethyl-alcoholic solutions and obtained a curve changing in direction at three points corresponding to alcohol-water complexes.

Since the significant points of the curves now recorded vary with temperature and differ for the two nitrophenols, there is no evidence for the existence of alcohol hydrates in the solutions. It is more probable that the points are of eutectic character. In view of the results obtained by McCombie and his co-workers (*loc. cit.*), it is

a remarkable coincidence that so many of the significant points in Figs. 1 and 2 occur where the alcohol and water in the solvent are in simple molecular proportion, as Table XIII shows.

TABLE XIII.

Fig 1.					
Point .....	H	J	P	O	R
EtOH, % .....	46	72	36	42	63
Ratio EtOH:H <sub>2</sub> O	1:3.00	1:0.993	2:9.08	2:7.06	2:3.00
Fig. 2.					
Point .....	D	F	K	J	M
EtOH, % .....	51	70	41	45	72
Ratio EtOH:H <sub>2</sub> O	2:4.91	1:1.09	2:7.23	1:3.12	1:0.993
Point .....	Q	P	S	V	Y
EtOH, % .....	27	39	56	33.8	39.0
Ratio EtOH:H <sub>2</sub> O	1:6.91	1:4.00	1:2.00	1:5.00	1:4.00

Although the presence of alcohol-water complexes in the solvent is improbable, it seems necessary to assume that *m*- and *p*-nitrophenols are both capable of association with the solvent. This especially applies to the co-existence of two saturated liquids along, *e.g.*, the straight line NP for 25° in Fig. 1. In this case, if the solvent used is 24% in alcoholic content, it will be induced, by addition of *m*-nitrophenol, to act as an equilibrium mixture of 15% alcohol (point N) and of 36% alcohol (point P), and with the requisite amount of *m*-nitrophenol, it will produce the two saturated liquid phases. The results found for the line NP agree with those calculated from the foregoing assumption, and this applies to the corresponding sections of the other curves.

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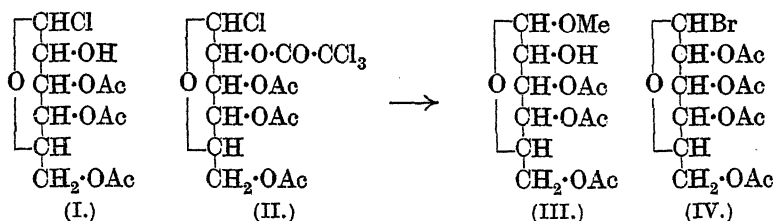
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### CLXXIII.—Glucosides. Part III. The Abnormal Replacement of Halogen in Glucosyl Halides: The Formation of $\beta$ -Glucosides from $\beta$ -Glucosyl Chlorides.

By WILFRED JOHN HICKINBOTTOM.

IN continuation of previous work on the formation of glucosides from  $\beta$ -glucosyl chlorides (J., 1929, 1676), the action of sodium alkoxides on 2-trichloroacetyl 3:4:6-triacetyl  $\beta$ -glucosyl chloride (II) and on 3:4:6-triacetyl  $\beta$ -glucosyl chloride (I) has been examined. It would be expected, by analogy with the behaviour of 2:3:4:6-tetra-acetyl  $\alpha$ -glucosyl bromide (IV) towards similar reagents (compare Zemplén and Kunz, *Ber.*, 1923, 56, 1710), that glucoside formation would occur with the normal change in con-

figuration. Indeed, Pictet and Castan (*Helv. Chim. Acta*, 1921, 4, 319) have stated that the glucosyl chloride, prepared by the addition of hydrogen chloride to  $\alpha$ -glucosan—and identified by them as  $\beta$ -glucosyl chloride, since its tetra-acetate has the same melting point as Fischer and Armstrong's labile 2 : 3 : 4 : 6-tetra-acetyl  $\beta$ -glucosyl chloride—gives  $\alpha$ -methylglucoside by reaction with a solution of sodium methoxide in methyl alcohol.



It was found, however, that  $\beta$ -glucosides were the principal products of the action of sodium alkoxides on 3 : 4 : 6-triacetyl  $\beta$ -glucosyl chloride and on 2-trichloroacetyl 3 : 4 : 6-triacetyl  $\beta$ -glucosyl chloride. These results are in direct contrast to the behaviour of the same  $\beta$ -glucosyl chlorides towards alcohols in presence of silver oxide or carbonate, or silver nitrate and pyridine. For comparison, the results are summarised in the following table :

*2-Trichloroacetyl 3 : 4 : 6-triacetyl  $\beta$ -glucosyl chloride.*

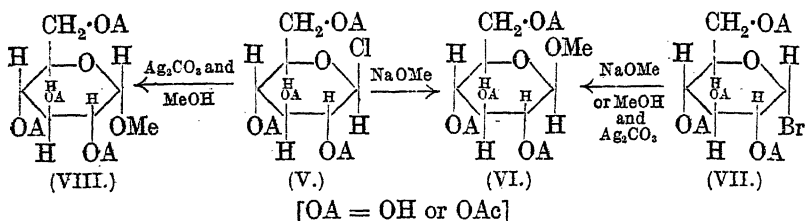
	Experimental conditions.	$\alpha$ - and $\beta$ -Glucosides, % in product.	
		$\alpha$ .	$\beta$ .
{ Brigl and Keppler ( <i>Ber.</i> , 1926, 59, 1588) Hickinbottom ( <i>loc. cit.</i> ) Hickinbottom ( <i>loc. cit.</i> )	Methyl alcohol and $\text{Ag}_2\text{O}$ or $\text{Ag}_2\text{CO}_3$	70	30
	Methyl alcohol, $\text{AgNO}_3$ , and pyridine	90	10
	Methyl alcohol and $\text{NaOMe}$	15	85
	Ethyl alcohol and $\text{NaOEt}$	10	90

*3 : 4 : 6-Triacetyl  $\beta$ -glucosyl chloride.*

Hickinbottom ( <i>loc. cit.</i> ) " " " "	Methyl alcohol and $\text{Ag}_2\text{O}$ or $\text{Ag}_2\text{CO}_3$	70	30
	Methyl alcohol, $\text{AgNO}_3$ , and pyridine	80	20
	Methyl alcohol and $\text{NaOMe}$	Approx. 100	

It is possible, therefore, to obtain either the  $\alpha$ - or the  $\beta$ -glucoside from each of these glucosyl chlorides by selecting the appropriate conditions. On current conceptions, it is assumed that, in the usual replacement of halogen in glucosyl halides by the action of silver carbonate and alcohol, a change in configuration occurs

(VI and VIII). This applies both to the  $\alpha$ - and to the  $\beta$ -series of glucosyl halides. It is then remarkable to find that both series of glucosyl halides yield glucosides of the same configuration by reaction with sodium alkoxides in alcohols. For instance, sodium methoxide in methyl alcohol produces  $\beta$ -methylglucosides (VI) from the  $\beta$ -glucosyl chlorides (V) used in the present investigation and also from 2:3:4:6-tetra-acetyl  $\alpha$ -glucosyl bromide (VII).



These observations appear to find a parallel in the behaviour of the  $\alpha$ - and  $\beta$ -penta-acetyl glucoses, which normally give the same tetra-acetyl glucosyl halide by the action of hydrogen halides. It is certain, when hydrogen chloride is used, that the first products have different configurations, but under the experimental conditions 2:3:4:6-tetra-acetyl  $\beta$ -glucosyl chloride isomerises to the more stable  $\alpha$ -glucosyl chloride (Schlubach, Stadler, and Wolf, *Ber.*, 1928, 61, 293; compare Fischer and Armstrong, *Ber.*, 1901, 34, 2894).

A somewhat similar explanation may account for the anomalous formation of  $\beta$ -glucosides from  $\beta$ -glucosyl chlorides, namely, that by the action of the sodium alkoxides the  $\beta$ -glucosyl chlorides are isomerised to  $\alpha$ -glucosyl chlorides, which then react in the normal way to give  $\beta$ -glucosides. This explanation was advanced by Fischer and Armstrong (*loc. cit.*) to account for the non-formation of  $\alpha$ -phenylglucoside from the unstable 2:3:4:6-tetra-acetyl  $\beta$ -glucosyl chloride. Their view was supported by the observation that the  $\beta$ -glucosyl chloride was converted completely into the  $\alpha$ -glucosyl chloride in an ethereal solution in contact with powdered hydrated sodium carbonate, or the wet sodium compound of glucose.

It appears at first sight that the extension of this hypothesis to account for the formation of  $\beta$ -glucosides from the  $\beta$ -glucosyl chlorides examined in the present work would be justifiable. A fuller consideration of the experimental facts, however, indicates that it can only be accepted if certain assumptions are made.

Although no accurate determinations of the velocity of the reaction between sodium methoxide or ethoxide and 2-trichloro-acetyl 3:4:6-triacetyl  $\beta$ -glucosyl chloride have been made owing



to the occurrence of comparatively slow side reactions, qualitative observations of the density of the precipitate of sodium chloride obtained when the reaction is carried out in ethyl alcohol indicate that glucoside formation occurs very quickly, and for 0.5*N*-solutions it is practically complete within a few minutes after mixing. Evidently, if the isomerisation hypothesis of Fischer and Armstrong holds, isomerisation must be complete or almost so before any replacement occurs; the isomerisation must therefore be extremely rapid. 2-Trichloroacetyl 3 : 4 : 6-triacetyl  $\beta$ -glucosyl chloride, however, is comparatively stable and does not isomerise readily. For instance, it does not change in non-hydroxylic solvents which bring about the conversion of 2 : 3 : 4 : 6-tetraacetyl  $\beta$ -glucosyl chloride into the  $\alpha$ -isomeride. Further, the addition of a trace of a methyl-alcoholic solution of sodium methoxide to an acetone solution of 2-trichloroacetyl 3 : 4 : 6-triacetyl  $\beta$ -glucosyl chloride does not cause any change of rotation over a period of 25 minutes. A drop of 20% aqueous sodium hydroxide added to an acetone solution of the  $\beta$ -glucoside brings about a change of  $[\alpha]_D$  only from  $+8^\circ$  to  $+13^\circ$  after 48 hours at room temperature. Further, a xylene solution of the  $\beta$ -glucosyl chloride may be kept in contact with an excess of dry, finely powdered sodium methoxide (free from methyl alcohol) at room temperature for 20 hours without any marked change in the rotation or without any serious amount of glucoside formation; indeed the greater part of the  $\beta$ -glucosyl chloride may be recovered unchanged. Micheel and Micheel (*Ber.*, 1930, 63, 392) have shown that anhydrous trimethylamine has no action on 2-trichloroacetyl 3 : 4 : 6-triacetyl  $\beta$ -glucosyl chloride in benzene at room temperature, and only a small action after 4 hours' heating at  $100^\circ$ .

The alcohol does not appear to be responsible for the isomerisation, since the rate of change of rotation in methyl alcohol is slow compared with the rate of replacement of the halogen (Hickinbottom, *loc. cit.*).

If the isomerisation hypothesis is to be retained, there must be assigned to the sodium alkoxide in the alcohol a catalytic power which is not possessed by the dry alkoxide, nor by the alcohol alone, nor by small quantities of the alcoholic methoxide in acetone.

An alternative hypothesis is to assume that addition to the glucosyl chloride may occur, and that the subsequent behaviour of the compound formed is determined by such factors as electron distribution, polarity, and steric configuration as well as by the relative energies of the systems.

It is known that the relative proportions of  $\alpha$ - and  $\beta$ -glucosides obtained by the replacement of the halogen of the glucosyl halides

may be varied very considerably. For instance, although sodium alkoxides react with 2-trichloroacetyl 3:4:6-triacetyl  $\beta$ -glucosyl chloride to give  $\beta$ -glucosides, sodium phenoxide gives a comparatively high proportion of the  $\alpha$ -phenylglucoside—approximately 60% of the total product.

When glucoside formation is effected from 2-trichloroacetyl 3:4:6-triacetyl  $\beta$ -glucosyl chloride or 3:4:6-triacetyl  $\beta$ -glucosyl chloride in an alcoholic suspension of silver oxide or silver carbonate, the product obtained is  $\alpha$ -glucoside with about 30% of  $\beta$ ; the proportion of  $\alpha$  can be increased if the silver carbonate is replaced by silver nitrate and pyridine. Further, it is possible to obtain some  $\alpha$ -glucosides from 2:3:4:6-tetra-acetyl  $\alpha$ -glucosyl bromide by reaction in presence of quinoline, the formation of  $\alpha$ -glucoside being apparently determined by the nature of the hydroxy-compound reacting.

These facts, together with observations on the opening of the ethylene-oxide ring in 3:4:6-triacetyl glucose anhydride, indicate that the reagents employed to effect glucoside formation determine, to some extent at least, the nature of the product.

Although it would be possible to explain these results by assuming that each reagent has its own isomerising effect, it seems more probable that the effect is determined by some factor such as preliminary addition.

In the reaction between sodium methoxide or ethoxide and 2-trichloroacetyl 3:4:6-triacetyl  $\beta$ -glucosyl chloride in equimolecular proportion in alcoholic solution, the trichloroacetyl group is split off and a 3:4:6-triacetyl  $\beta$ -alkylglucoside (III) is produced. This reaction provides an alternative method of preparing these compounds, which hitherto have only been obtained from 3:4:6-triacetyl  $\beta$ -glucosyl chloride or by the reaction of 3:4:6-triacetyl glucose anhydride with alcohols. It is an additional example of the comparative instability of the trichloroacetyl group in position 2 (Brigl, *Z. physiol. Chem.*, 1921, **116**, 1; Hickinbottom, *loc. cit.*).

#### EXPERIMENTAL.

*Action of Sodium Methoxide in Methyl Alcohol on 2-Trichloroacetyl 3:4:6-Triacetyl  $\beta$ -Glucosyl Chloride.—Formation of 3:4:6-triacetyl  $\beta$ -methylglucoside.* The sodium methoxide used in these experiments was prepared by dissolving sodium in freshly distilled, dry methyl alcohol to yield an approximately 0.5*N*-solution. The concentration was determined accurately by titration against standard acid.

A measured volume of this solution, diluted with methyl alcohol,

was added to 2-trichloroacetyl 3 : 4 : 6-triacetyl  $\beta$ -glucosyl chloride so that the glucosyl chloride and sodium methoxide were present in equimolecular proportion. The changes in specific rotation (calc. on the glucosyl chloride) were as follows ( $c = 5.23$ ;  $l = 2$ ) :

$t$ (mins.) ...	2	3	4	8	14	42	62	88
$[\alpha]_D^{25}$ .....	+27.3°	28.8°	27.3°	26.8°	24.2°	20.7°	19.2°	20.0° (const.)

A number of other determinations of the change of rotation, also made at room temperature, were in general agreement with those recorded above:  $[\alpha]_D +27-30^\circ$  about 2 minutes after mixing, changing to a constant end value between  $+14^\circ$  and  $+25^\circ$ .

The solutions obtained were clear and neutral to moist litmus. Evaporation under diminished pressure at room temperature, followed by repeated extraction of the residue with boiling chloroform to eliminate inorganic salts, and subsequent evaporation of the chloroform, yielded the product of the reaction as a colourless transparent gum. It slowly solidified in a vacuum desiccator to a crystalline mass (A).

The inorganic residue remaining after the extraction with chloroform was sodium chloride. In one or two experiments it contained a small quantity of acetate.

The crystalline mass (A) was not entirely free from lower-melting compounds. The products from two typical experiments showed  $[\alpha]_D +32.7^\circ$  ( $c = 1.65$ ) and  $[\alpha]_D +37.6^\circ$  ( $c = 1.78$ ) in ethyl alcohol. On deacetylation with alcoholic ammonia a mixture of  $\alpha$ - and  $\beta$ -glucosides resulted. From the two specimens for which the specific rotations are recorded above, methylglucosides were obtained which, after removal of amides and drying at  $78^\circ/12$  mm., had  $[\alpha]_D -6^\circ$  ( $c = 1.38$ ) and  $[\alpha]_D +4^\circ$  ( $c = 2.63$ ) in water. These values correspond to mixtures of  $\beta$ -methylglucoside containing 14% and 19% respectively of  $\alpha$ -methylglucoside. Crystallisation of the crude glucoside from alcohol furnished pure  $\beta$ -methylglucoside,  $[\alpha]_D -32^\circ$  in water ( $c = 1.07$ ), m. p.  $107-108^\circ$  (alone or mixed with a genuine specimen of  $\beta$ -methylglucoside). The presence of  $\alpha$ -methylglucoside was established by adding ether to a concentrated alcoholic solution of the product of deacetylation of the crude product (A). Two forms of crystal, which could be separated mechanically, were deposited on keeping. The greater part consisted of stout transparent prisms of  $\beta$ -methylglucoside. A few aggregates of small needles were also present, and after further purification from absolute alcohol these were identified as  $\alpha$ -methylglucoside by melting point and rotation.

*Isolation of 3 : 4 : 6-triacetyl  $\beta$ -methylglucoside (III).* Extraction of the solid (A) with ether left a gummy residue which showed

little sign of crystallising. The ethereal solution on slow spontaneous evaporation deposited aggregates of prismatic needles, which after crystallisation from carbon tetrachloride or alcohol were obtained pure; m. p. 93—94°,  $[\alpha]_D +20^\circ$  in ethyl alcohol ( $c = 4.5$ ) (Found: C, 49.0; H, 6.4; OMe, 9.6. Calc. for  $C_{13}H_{20}O_9$ : C, 48.6; H, 6.4; OMe, 9.6%). The analysis corresponds to triacetyl methylglucoside, and the constants are in good agreement with those recorded for 3:4:6-triacetyl  $\beta$ -methylglucoside prepared from 3:4:6-triacetyl glucose anhydride (Hickinbottom, J., 1928, 3144). The substance did not depress the melting point of an authentic specimen of 3:4:6-triacetyl  $\beta$ -methylglucoside, and yielded 2:3:4:6-tetra-acetyl  $\beta$ -methylglucoside on acetylation.

*Action of an Excess of Sodium Methoxide in Methyl Alcohol on 2-Trichloroacetyl 3:4:6-Triacetyl  $\beta$ -Glucosyl Chloride.*—A freshly prepared solution (0.404*N*) of sodium methoxide (1.154 mols.) in dry methyl alcohol was added to 2-trichloroacetyl 3:4:6-triacetyl  $\beta$ -glucosyl chloride (0.5421 g.; 1 mol.). The solution was rapidly diluted with dry methyl alcohol to 25 c.c. The following changes in rotation at room temperature were observed ( $l = 2.0$ ;  $c = 2.17$ ):

$t$ (mins.)	2	4	6	10	12	14	17
$\alpha_D$	+0.94°	0.66°	0.45°	0.29°	0.25°	0.20°	0.13°
$t$ (mins.)	19	23	29	54	88	1080	
$\alpha_D$	+0.10°	0.03°	-0.10°	-0.28°	-0.35°	-0.54° (const.)	

The solution was neutral after 24 hours. The final value, calculated on the assumption that only  $\beta$ -methylglucoside is present, is  $[\alpha]_D -31.2^\circ$ .

The product obtained on evaporation, however, did not consist entirely of  $\beta$ -methylglucoside. After solution of the glucosides in absolute alcohol and filtration to remove mineral matter, no appreciable amount of  $\beta$ -methylglucoside could be separated, even after concentration of the alcoholic solution and nucleation with  $\beta$ -methylglucoside. A determination of the acetyl content by hydrolysis with alcoholic potash showed that the product consisted largely of monoacetyl  $\beta$ -methylglucoside (Found: Ac, 13.2. Calc. for  $C_7H_{13}O_6Ac$ : Ac, 18.4%). It is evident that extensive deacetylation is brought about even in the cold by the action of a slight excess of sodium methoxide.

*Action of a Solution of Sodium Ethoxide in Ethyl Alcohol on 2-Trichloroacetyl 3:4:6-Triacetyl  $\beta$ -Glucosyl Chloride.*—The formation of 3:4:6-triacetyl  $\beta$ -ethylglucoside. The  $\beta$ -glucosyl chloride (1.1393 g.) was mixed with sodium ethoxide (1 mol.) in ethyl alcohol at room temperature, and the solution diluted to 25 c.c. No readings of the change of rotation were taken owing to the precipit-

ation of sodium chloride. After 24 hours, the solution was neutral to moist litmus, and after filtration had  $\alpha_D + 0.21^\circ$  ( $l = 0.5$ ); hence  $[\alpha]_D + 9^\circ$ , calculated on the glucosyl chloride, or  $[\alpha]_D + 11^\circ$ , calculated on triacetyl ethylglucoside.

Saturation of the solution with dry ammonia at room temperature, and subsequent evaporation after 20 hours, followed by extraction with ether to remove trichloroacetamide, and then drying at  $78^\circ/12$  mm., left a mixture of ethylglucosides,  $[\alpha]_D - 14^\circ$  in water ( $c = 1.95$ ;  $l = 0.5$ ). The solution was almost indifferent to Fehling's solution, and showed no detectable mutarotation after 24 hours. This value of the specific rotation corresponds to a mixture of 91% of  $\beta$ -ethylglucoside and 9% of  $\alpha$ -ethylglucoside. The presence of  $\beta$ -ethylglucoside as the major constituent of the mixture was also demonstrated by acetylation, whereby 2:3:4:6-tetra-acetyl  $\beta$ -ethylglucoside was obtained which, after one crystallisation from alcohol, melted, alone or mixed with a genuine specimen, at  $103-104^\circ$ .

*Isolation of 3:4:6-triacetyl  $\beta$ -ethylglucoside.* The filtered solution resulting from the action of sodium ethoxide (1 mol.) on 2-trichloroacetyl 3:4:6-triacetyl  $\beta$ -glucosyl chloride in alcohol had  $[\alpha]_D + 4^\circ$  ( $c = 4.78$ ), calculated on the original glucosyl chloride, and  $[\alpha]_D + 6^\circ$ , calculated on triacetyl ethylglucoside. It was evaporated under reduced pressure, and the dry residue extracted with ether. The ethereal solution deposited, on spontaneous evaporation, needles, m. p.  $105-110^\circ$ , which were contaminated by a small quantity of a substance having the odour of an ester. After three crystallisations from ethyl alcohol, the solid melted at  $119-120^\circ$ , and was identified by its m. p., mixed m. p., and specific rotation as 3:4:6-triacetyl  $\beta$ -ethylglucoside (Hickinbottom, *loc. cit.*).

*Action of Sodium Phenoxide and Phenol on 2-Trichloroacetyl 3:4:6-Triacetyl  $\beta$ -Glucosyl Chloride.*—Sodium phenoxide solution was prepared by the action of metallic sodium on an excess of molten phenol, precautions being taken to exclude moisture. The crystalline compound which separated on cooling, and probably consisted of the additive compound of phenol and sodium phenoxide (compare Gentsch, D.R.-P. 156761), was dissolved in sufficient dry acetone to give an approximately 0.5*N*-solution. The concentration of phenoxide was determined accurately by titration.

2-Trichloroacetyl 3:4:6-triacetyl  $\beta$ -glucosyl chloride (0.7816 g.) was treated with sodium phenoxide (1 mol.), and the solution made up to 25 c.c. with acetone. A precipitate of sodium chloride formed rapidly. After 2 hours the filtered solution had  $[\alpha]_D + 33^\circ$ , calculated on the basis of the glucosyl chloride, and this value did not alter during 48 hours. The filtered solution was evaporated, and

the residue heated at 100°/15 mm. to remove phenol. A brownish gum was obtained,  $[\alpha]_D +106.5^\circ$  in benzene ( $c = 2.16$ ;  $l = 0.5$ ). After deacetylation with alcoholic alkali, a mixture of phenylglucosides remained,  $[\alpha]_D +88^\circ$  in water ( $c = 1.48$ ;  $l = 0.5$ ). Acetylation of the glucosides gave a brownish mixture of the tetra-acetyl phenylglucosides,  $[\alpha]_D +95^\circ$  in benzene ( $c = 1.35$ ;  $l = 0.5$ ). This value corresponds to a mixture containing approximately 64% of tetra-acetyl  $\alpha$ -phenylglucoside and 36% of the  $\beta$ -isomeride. Crystallisation of the crude mixture from alcohol furnished pure 2:3:4:6-tetra-acetyl  $\alpha$ -phenylglucoside, m. p. 110–112° alone or mixed with an authentic specimen.  $[\alpha]_D +168^\circ$  in benzene.

*Action of a Solution of Sodium Methoxide in Methyl Alcohol on 3:4:6-Triacetyl  $\beta$ -Glucosyl Chloride.*—Sodium methoxide (1 mol.) in methyl-alcoholic solution (0.6683*N*) was diluted with methyl alcohol and added to 0.6655 g. of pure 3:4:6-triacetyl  $\beta$ -glucosyl chloride (m. p. 154°). The solution was made up to 25 c.c. as rapidly as possible: 4 minutes after mixing,  $[\alpha]_D$  (calc. on the glucosyl chloride) was  $-7.5^\circ$ , and it fell to a constant value of  $[\alpha]_D -22.5^\circ$  on keeping over-night at room temperature. The solution then contained no free glucosyl chloride. It was evaporated under diminished pressure, and the residue extracted repeatedly with boiling ethyl acetate. Evaporation of the extract left a transparent colourless gum which was inactive towards boiling Fehling's solution. Deacetylation of the gum with alcoholic ammonia at room temperature left a product which consisted very largely of  $\beta$ -methylglucoside,  $[\alpha]_D -32^\circ$  in water ( $c = 1.57$ ;  $l = 0.5$ ). The identification as  $\beta$ -methylglucoside was established by its m. p., mixed m. p., and specific rotation, after crystallisation from absolute alcohol.

*Action of Sodium Phenoxide on 3:4:6-Triacetyl  $\beta$ -Glucosyl Chloride.*—A solution (0.4161*N*) of sodium phenoxide (1 mol.) in acetone containing free phenol was added to 3:4:6-triacetyl  $\beta$ -glucosyl chloride (0.5364 g.), and the solution diluted rapidly to 25 c.c. The separation of sodium chloride commenced in less than a minute after mixing. Filtration after 18 hours gave a solution having  $[\alpha]_D +50^\circ$ , calculated on the basis of the glucosyl chloride. In another experiment, with 0.5031 g. of  $\beta$ -glucosyl chloride in 25 c.c. of acetone containing 1 mol. of sodium phenoxide, there resulted a solution which had  $[\alpha]_D +49^\circ$  after being kept for 50 hours at room temperature. Both solutions were faintly alkaline to moist litmus. They were combined, and the acetone was removed under reduced pressure. The residue, after being heated at 100°/15 mm. to remove phenol, was a light brown, transparent gum,  $[\alpha]_D +42^\circ$  in alcohol ( $c = 1.62$ ;  $l = 0.5$ ).

Acetylation of this residue in pyridine furnished a product having,

after the usual treatment to remove pyridine,  $[\alpha]_D + 40^\circ$  in benzene ( $c = 2.1$ ). This value corresponds to a mixture of approximately 65% of the tetra-acetyl  $\beta$ -phenylglucoside and 35% of the  $\alpha$ -isomeride. Crystallisation from alcohol gave pure 2:3:4:6-tetra-acetyl  $\beta$ -phenylglucoside, m. p. 125–126°,  $[\alpha]_D - 28^\circ$  in benzene.

*Action of Sodium Methoxide in Methyl Alcohol on 2:3:4:6-Tetra-acetyl  $\alpha$ -Glucosyl Bromide.*—In order to compare the behaviour of the  $\beta$ -glucosyl halides towards sodium methoxide with that of the  $\alpha$ -glucosyl halides the action of sodium methoxide in methyl alcohol on 2:3:4:6-tetra-acetyl  $\alpha$ -glucosyl bromide was followed polarimetrically.

Sodium methoxide (1 mol.) in methyl-alcoholic solution (0.4*N*) was added to 1.1969 g. of 2:3:4:6-tetra-acetyl  $\alpha$ -glucosyl bromide at room temperature, and methyl alcohol then added to make the volume up to 50 c.c. The changes in rotation were:

<i>t</i> (mins.) ...	1.5	3	5	8	45	1135
$\alpha_D$ ( $l = 0.5$ )	-0.01°	-0.05°	-0.07°	-0.09°	-0.13°	-0.15° (const.)

The solution after acetylation yielded tetra-acetyl  $\beta$ -methyl-glucoside.

*The Stability of 2-Trichloroacetyl 3:4:6-Triacetyl  $\beta$ -Glucosyl Chloride.*—Attempts were made to effect the isomerisation of 2-trichloroacetyl 3:4:6-triacetyl  $\beta$ -glucosyl chloride by the action of traces of alkali or sodium methoxide in acetone.

A solution of the  $\beta$ -glucosyl chloride in dry acetone ( $[\alpha]_D + 8^\circ$ ;  $c = 4.41$ ;  $l = 0.5$ ), treated with 2 drops of 0.5*N*-solution of sodium methoxide in methyl alcohol, showed no change in rotation after being kept at room temperature for 25 minutes. The subsequent addition of 1 drop of 5*N*-sodium hydroxide gave a solution which had  $[\alpha]_D + 10.5^\circ$  after 24.5 hours and  $[\alpha]_D + 13.1^\circ$  after 47.5 hours. The tube contained a small deposit, presumably sodium chloride. The solution, however, on evaporation gave unchanged  $\beta$ -glucosyl chloride.

A suspension of an excess of sodium methoxide (e.g., 2 mols.) in dry xylene free from methyl alcohol had only a slow action on 2-trichloroacetyl 3:4:6-triacetyl  $\beta$ -glucosyl chloride. After 17 hours, with intermittent shaking, the filtered solution had  $[\alpha]_D + 17^\circ$ , calculated on the basis of the glucosyl chloride. Evaporation under reduced pressure gave a residue which partly crystallised, and from which a large proportion of unchanged  $\beta$ -glucosyl chloride was isolated.

The addition of 1 drop of concentrated hydrochloric acid to an acetone solution of 2-trichloroacetyl 3:4:6-triacetyl  $\beta$ -glucosyl chloride ( $c = 4.4$ ) brought about a change in specific rotation from  $+7.2^\circ$  to  $+9.6^\circ$  after 92 hours. The solution had become

darker in colour. On evaporation it yielded a somewhat impure product, m. p. 120—125°, from which the pure  $\beta$ -glucosyl chloride, m. p. 135—136°, was obtained by one crystallisation from ethyl alcohol.

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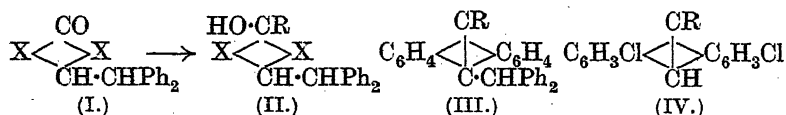
## CLXXIV.—*The Synthesis of meso-Alkyl and meso-Aryl Anthracene Derivatives. Part VII.*

By EDWARD DE BARRY BARNETT and NORMAN FREDERICK GOODWAY.

THE isolation of 3-chloro-9-anthrone (Barnett and Matthews, J., 1923, 2549) from the mixture of 2- and 3-chloro-9-anthrone obtained by the reduction of 2-chloroanthraquinone with tin and hydrochloric acid or with aluminium powder and concentrated sulphuric acid can be readily effected by the method used by Barnett and Goodway (J., 1929, 1754) for the isolation of 3-methyl-9-anthrone, *viz.*, acetylation and fractional crystallisation of the mixed anthranyl acetates.

2- and 3-Chloro-9-anthrone condense readily with benzyl chloride in the presence of potassium hydroxide and yield, as would be expected, the *chlorodibenzylanthrones*.

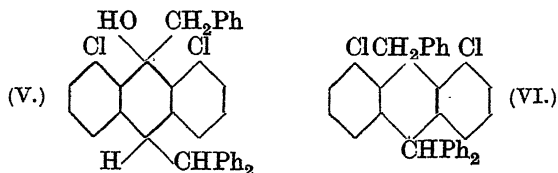
By interaction with magnesium alkyl halides (Barnett and Goodway, J., 1929, 20, 1745), 10-benzhydrylanthrone (I,  $X = C_6H_4$ ) gives dihydroanthranols (II,  $X = C_6H_4$ ) which undergo transannular loss of water to form the alkylbenzhydrylanthracenes (III), whereas 1 : 5-dichloro-10-benzhydrylanthrone (I,  $X = C_6H_3Cl$ ) gives dihydroanthranols (II,  $X = C_6H_3Cl$ ) which undergo transannular loss of benzhydrol to give the alkylanthracene (IV).



As it seemed possible that this difference in behaviour was due to the co-ordination of the hydrogen atom at 10 with the chlorine atom at 5 (compare Barnett and Wiltshire, *Ber.*, 1929, 62, 3063; Barnett, Goodway, and Wiltshire, *ibid.*, 1930, 63, 472), the behaviour of the dihydroanthranols obtained by the action of magnesium benzyl chloride on some other *Bz.*-chloro-10-benzhydrylanthrones has been examined. The results obtained, which are summarised below, show that co-ordination of the *meso*-hydrogen atom cannot possibly

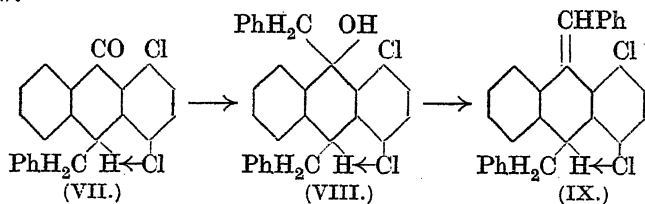


be the factor determining the type of transannular loss suffered under the influence of hydrogen ions: for instance, 1-chloro-, 2-chloro-, 4-chloro-, 1:4-dichloro-, and 4:5-dichloro-9-benzyl-10-benzhydryl-9:10-dihydro-9-anthranol all underwent loss of benzhydrol and yielded the corresponding chlorinated 9-benzylanthrane; 1:8-dichloro-9-benzyl-10-benzhydryl-9:10-dihydro-9-anthranol (V), on the other hand, lost water and passed into 1:8-dichloro-9-benzyl-10-benzhydrylanthrane (VI).



1:8- and 4:5-Dichloro-9-anthrone differ markedly from anthrone itself in their behaviour towards benzophenone chloride, for whereas anthrone yields diphenylmethyleanthrone (anthrafuchsone) (Padova, *Compt. rend.*, 1906, **143**, 121; *Ann. Chim.*, 1910, **19**, 388), the two dichloroanthrones are merely oxidised to the dianthrones. Also, after boiling for 3 hours with phthaloyl chloride in xylene solution, they were largely recovered unchanged and, although some resinous matter was formed in each case, no compound corresponding to the phthalylidene derivative obtained by Padova (*Compt. rend.*, 1909, **418**, 290) from anthrone itself could be detected.

As was foreseen, 1:4-dichloroanthrone condenses with benzyl chloride in the presence of sodium hydroxide to give 1:4-dichloro-10-benzylanthrone (VII), and the dihydroanthranol (VIII) obtained from this by the action of magnesium benzyl chloride undergoes loss of water to form the benzylidene derivative (IX). This behaviour is in harmony with the suggestion (Barnett, Goodway, and Wiltshire, *loc. cit.*) that a *meso*-hydrogen atom forms a chelate ring with the chlorine atom in the *peri*-position, as indicated in the formulæ below.



The failure of 1:4-dichloro-10-benzylanthrone to undergo enolisation when boiled with alcoholic sodium hydroxide furnishes further evidence of the immobilisation of the *meso*-hydrogen atom.

## EXPERIMENTAL.

**3-Chloro-9-anthrone.**—The mixture of anthrones obtained by the reduction of 2-chloroanthraquinone by the tin-hydrochloric acid method was acetylated on the water-bath with pyridine and acetic anhydride and the resulting anthranyl acetates were recrystallised from benzene-light petroleum or toluene-light petroleum. 3-Chloro-9-anthranyl acetate (m. p. 146°; Barnett and Wiltshire, J., 1928, 1822) was thus easily obtained in the pure state; it yielded the corresponding anthrone on hydrolysis with alcoholic alkali in an inert atmosphere (compare Barnett and Goodway, J., 1929, 1754).

**2-Chloro-10:10-dibenzylanthrone.**—2-Chloro-9-anthrone (10 g.) and benzyl chloride (10 c.c.) were boiled under reflux with a solution of potassium hydroxide (7 g.) in water (25 c.c.) for an hour. After being washed with water and with ice-cold ether, the product was recrystallised from glacial acetic acid and from benzene-light petroleum. It was then colourless and melted at 185° (Found: C, 82.0; H, 5.3.  $C_{23}H_{21}OCl$  requires C, 82.2; H, 5.1%).

**3-Chloro-10:10-dibenzylanthrone**, prepared in exactly the same way as the above compound, formed colourless crystals, m. p. 174° (Found: C, 82.3; H, 5.4%).

**Bz.-Chloro-10-benzhydrylanthrones.**—In all cases the anthrone (5–10 g.) was boiled with an excess of crude benzhydryl chloride (10–20 c.c.) and aqueous sodium hydroxide (75–100 c.c.; about 12% strength) until the black tar at first formed vanished (10–30 minutes). After cooling, the viscous product was washed with water, triturated with ice-cold ether to remove resinous by-products, and crystallised from acetic acid or acetone and then from benzene-light petroleum. The products were all colourless and, when boiled with alcoholic alkali, gave a distinct colour only when there was no chlorine atom in position 4 or 5.

In the following table the figures under "Analysis" refer to carbon and hydrogen, the calculated figures being given in parentheses.

Cl at	M. p.	Analysis.	Cl at	M. p.	Analysis.
1	204°	82.3; 5.0 (82.1; 4.8)	1:4	191°	75.4; 4.4 (75.5; 4.2)
2	171	82.1; 5.0 " "	1:8	242	75.4; 4.4 " "
4	175	82.0; 4.8 " "	4:5	224	75.4; 4.3 " "

A crystalline product could not be isolated from the resin obtained when 3-chloro-9-anthrone was boiled with benzhydryl chloride and alkali.

**Bz.-Chloro-9-benzyl-10-benzhydryl-9:10-dihydro-9-anthranols.**—In all cases the benzhydrylanthrone was added slowly to an ethereal solution of magnesium benzyl chloride (3 mols.) cooled in a freezing mixture, and after being kept over-night at the ordinary temperature the whole was poured on a mixture of ice and solid ammonium

chloride. Sparingly soluble dihydroanthranols were isolated by filtration, and the more soluble dihydroanthranols by evaporation of the washed and dried ( $\text{Na}_2\text{SO}_4$ ) ethereal solution. In the latter case the dihydroanthranol was sometimes left as an oil which became solid on treatment with aqueous acetone or light petroleum, but the dihydroanthranol obtained from 1-chloro-10-benzhydryl-anthrone refused to crystallise. Purification was effected by recrystallisation from aqueous acetone and then from benzene-light petroleum. The products were all colourless.

Dehydration was brought about by means of acetic acid containing a little concentrated hydrochloric acid, either by keeping over-night at the ordinary temperature or by brief heating on the water-bath. The resulting *Bz.*-chloro-9-benzylantracenes were identified by direct comparison with authentic specimens.

Cl at	M. p.	Analysis.	Cl at	M. p.	Analysis.
2	166°	83.8; 5.7 (83.9; 5.6)	1:4	199°	78.2; 5.2 (78.3; 5.0)
4	208	83.6; 5.8 „ „	1:8	190	78.4; 5.3 „ „
			4:5	186	78.5; 5.1 „ „

1:8-Dichloro-9-benzyl-10-benzhydrylanthrane (VI) formed pale yellow crystals, m. p. 139°, from acetone (Found: C, 81.1; H, 4.8.  $\text{C}_{34}\text{H}_{24}\text{Cl}_2$  requires C, 81.1; H, 4.8%).

*Action of Benzophenone Chloride on 1:8- and 4:5-Dichloro-anthrone.*—The anthrone (5.4 g.) was boiled for 3 hours with benzophenone chloride (5.5 g.) and xylene (50 c.c. in the case of 1:8-dichloroanthrone; 15 c.c. in the case of 4:5-dichloroanthrone). 1:8:1':8'-Tetrachloro-10:10'-dianthrone separated from the boiling solution, and after being washed with xylene was recrystallised from nitrobenzene (Found: C, 64.0; H, 2.7. Calc.: C, 64.1; H, 2.7%). 4:5:4':5'-Tetrachloro-10:10'-dianthrone was isolated by the addition of light petroleum and subsequent recrystallisation from benzene-ethyl acetate. On heating, it darkened but did not melt below 315° (compare Barnett, Cook, and Matthews, *Rec. trav. chim.*, 1926, 45, 75).

Neither of the above dianthrone gave any colour on boiling with alcoholic alkali. The latter, however, was enolised by pyridine and after boiling for 3 minutes with this solvent gave an immediate red colour on the addition of a drop of sodium hydroxide. The former gave no colour after similar treatment, presumably owing to the immobilisation of the *meso*-hydrogen atoms by co-ordination with the chlorine atoms.

1:4-Dichloro-10-benzyl-9-anthrone (VII).—1:4-Dichloroanthrone (10 g.) was boiled with benzyl chloride (10 c.c.) and a solution of potassium hydroxide (7 g.) in water (30 c.c.) for an hour. The product having been washed with water and freed from volatile

material by distillation with steam, the resinous residue was triturated with cold ether and crystallised from benzene-light petroleum. The resulting colourless crystals melted at  $123^{\circ}$  (Found: C, 71.3; H, 4.1.  $C_{21}H_{14}OCl_2$  requires C, 71.4; H, 4.0%).

1:4-Dichloro-9:10-dibenzyl-9:10-dihydroanthranol (VIII).—1:4-Dichloro-10-benzylanthrone (6 g.) was added slowly to an ethereal solution of magnesium benzyl chloride (3 mols.) cooled in a freezing mixture, and the whole kept over-night at the ordinary temperature and then poured on a mixture of ice and solid ammonium chloride. The oil obtained by evaporation of the washed ethereal solution became solid on cooling and was then recrystallised from aqueous acetone and from benzene-light petroleum. The resulting colourless crystals melted at  $165^{\circ}$  (Found: C, 75.5; H, 5.1.  $C_{28}H_{22}OCl_2$  requires C, 75.5; H, 4.9%).

1:4-Dichloro-10-benzylidene-9:10-dihydroanthracene (IX).—The above dihydroanthranol was kept over-night at the ordinary temperature in glacial acetic acid solution to which a little concentrated hydrochloric acid had been added. The resulting solid separated from benzene-light petroleum in colourless non-fluorescent crystals, m. p.  $186^{\circ}$  (Found: C, 78.7; H, 4.9.  $C_{28}H_{20}Cl_2$  requires C, 78.7; H, 4.7%).

One of the authors (E. de B. B.) desires to express his thanks to Imperial Chemical Industries, Ltd., for a gift of 1:8-dichloro-anthraquinone and for a grant out of which some of the expenses of this research have been paid.

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## CLXXV.—The Space Configuration of the Trithioacetaldehydes.

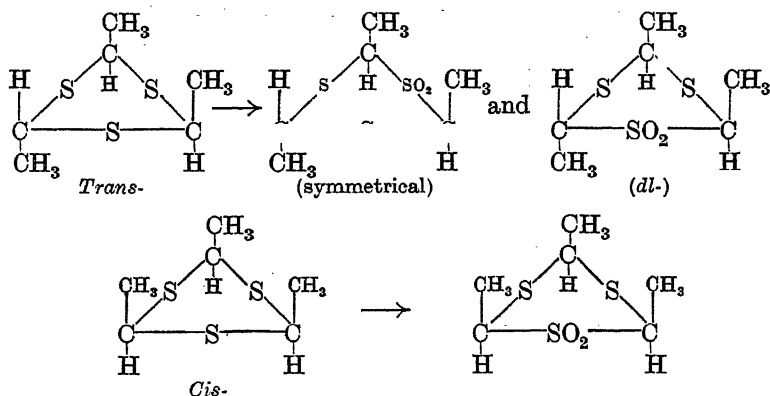
By FREDERICK DANIEL CHATTAWAY and EDWIN GEOFFREY  
KELLETT.

RECENT work (Fromm and Engler, *Ber.*, 1925, 58, 1916; Bell, Bennett, and Mann, J., 1929, 1462) has supported the earlier view of Baumann and Fromm (*Ber.*, 1889, 22, 2600) that trithioacetaldehyde,  $(CH_3 \cdot CH:S)_3$ , exists in two isomeric forms, the so-called  $\alpha$ -trithioacetaldehyde, m. p.  $101^{\circ}$ , and  $\beta$ -trithioacetaldehyde, m. p.  $126^{\circ}$ , and that the supposed  $\gamma$ -form (Marckwald, *Ber.*, 1886, 19, 1826; Polack and Thummel, *Ber.*, 1889, 22, 2871; Mann and Pope, J., 1923, 123, 1178) is a mixture of these two. Although it has been customary to regard the  $\alpha$ -form as the *cis*-isomeride

(having all three methyl groups on the same side of the plane of the ring), there is no direct chemical evidence for this view. Baumann and Fromm regarded the  $\beta$ -form as *trans*- (Ber., 1891, 24, 1428) because it is the more stable isomeride, arguing by analogy with the hexahydrophthalic acids. Auwers and Ottens (Ber., 1924, 57, 439) support this view from comparisons of physical data.

The oxidation products of these two isomerides which have previously been described are anomalous in that both isomerides give one and the same trisulphone (Baumann and Fromm, Ber., 1889, 22, 2606; Lomnitz, Ber., 1894, 27, 1667) and one and the same disulphone (Baumann and Fromm, Ber., 1893, 26, 2074); while only one trisulphoxide of  $\alpha$ -trithioacetaldehyde and one of the  $\beta$ -form have been obtained (Fromm and Engler, *loc. cit.*), though the stereoisomeric possibilities, having regard to the possible dispositions of the semipolar double bonds in relation to the plane of the ring (compare Bell and Bennett, J., 1927, 1798), are much more numerous than this (six trisulphoxides of the *trans*-form, and four of the *cis*-form, may be predicted).

It is shown in the present paper that  $\alpha$ -trithioacetaldehyde forms *two* isomeric monosulphoxides, and  $\beta$ -trithioacetaldehyde *one*. The maximum number theoretically possible is *two* from the *cis*-form and *four* from the *trans*-form. Each of the three monosulphoxides actually obtained has, however, been further oxidised to a distinct monosulphone. Hence, since  $\alpha$ -trithioacetaldehyde yields two isomeric monosulphones, and the  $\beta$ -form only one, the  $\alpha$ -form must have the *trans*-structure.



#### EXPERIMENTAL.

*Oxidation of  $\beta$ -Trithioacetaldehyde to a Monosulphoxide.*—10 G. of finely powdered  $\beta$ -trithioacetaldehyde, m. p. 126°, were suspended

in 100 c.c. of glacial acetic acid, and 6 c.c. of "perhydrol," dissolved in 150 c.c. of acetic acid, added during 8 hours, with vigorous shaking. (The reaction is rapid, since 15 minutes after addition of the last drop of "perhydrol" solution no free hydrogen peroxide could be detected in the reaction mixture by the perchromic acid test.) The clear solution thus obtained was diluted to 1500 c.c. with cold water and 220 g. of anhydrous sodium carbonate were added; it was then filtered, and the filtrate extracted with 400 c.c. of chloroform in eight portions. The extract was dried over calcium chloride and the chloroform evaporated, leaving 9.5 g. of crude product. On crystallisation from 20% aqueous alcohol (60 c.c.), this proved to be a single pure compound.

*β-Trithioacetaldehyde monosulphoxide* crystallises from alcohol, in which it is very readily soluble, in large, compact, colourless crystals of ill-defined shape, m. p. 118.5° (Found: S, 49.2.  $C_6H_{12}OS_3$  requires S, 49.1%). It is moderately easily soluble in cold water, and readily soluble in all the usual organic solvents. On warming with zinc dust in dilute hydrochloric acid, it is reduced to *β*-trithioacetaldehyde.

*Oxidation of β-Trithioacetaldehyde Monosulphoxide to a Monosulphone.*—3 G. of potassium permanganate, dissolved in 300 c.c. of water, were added during 6 hours to a stirred solution of 5.6 g. of *β*-trithioacetaldehyde monosulphoxide in 750 c.c. of water containing 10 g. of magnesium sulphate. Each drop of permanganate was decolorised almost instantaneously. When all had been added, the precipitated manganese dioxide was dissolved by passing sulphur dioxide through the mixture. The resulting liquor, containing the product partly in suspension and partly in solution, was extracted with 120 c.c. of chloroform in eight portions. The extract was dried and evaporated, and the residue recrystallised from 50% aqueous alcohol (yield, 4 g.).

*β-Trithioacetaldehyde monosulphone* crystallises from alcohol, in which it is moderately easily soluble, in slender colourless prisms, m. p. 190° (Found: S, 45.6.  $C_6H_{12}O_2S_3$  requires S, 45.3%). It is only sparingly soluble in cold water. It is not reduced by zinc in hydrochloric acid, nor by tin in a mixture of hot hydrochloric and acetic acids, nor by hydriodic acid in the cold. On boiling for some time with fresh, constant-boiling hydriodic acid, it is to some extent decomposed, hydrogen sulphide being liberated and tarry products formed; any crystallisable product recovered from this reaction, however, is the unchanged sulphone.

It may be noted (a) that *β*-trithioacetaldehyde is not oxidised by "perhydrol" in neutral acetone solution, (b) that, if it is attempted to oxidise *β*-trithioacetaldehyde directly to its lower oxidation

products with a limited amount of either neutral or acid permanganate, a complex mixture of products is formed, even though the process be protracted over several days, and (c) that, if it is attempted to oxidise  $\beta$ -trithioacetaldehyde monosulphoxide with a limited amount of acid permanganate, a complex mixture of products is again obtained.

*Oxidation of  $\alpha$ -Trithioacetaldehyde to a Pair of Isomeric Monosulphoxides.*—10 G. of  $\alpha$ -trithioacetaldehyde, m. p.  $100^\circ$ , were suspended in 75 c.c. of acetic acid and oxidised with "perhydrol" as above. Yield of crude product, 9.5 g. This was recrystallised from 20% aqueous alcohol (75 c.c. for the first operation) until it had a constant m. p.  $136^\circ$  (4.6 g.). The mother-liquors were concentrated on the water-bath and evaporated to dryness in a vacuum desiccator. The residue was extracted by rinsing it several times with quantities of 25 c.c. of water at  $50^\circ$ ; these extracts were evaporated to dryness and the residue was recrystallised from 10% aqueous alcohol until it had m. p.  $93^\circ$  (1 g.).

$\alpha$ -Trithioacetaldehyde  $\alpha$ -monosulphoxide crystallises from 20% alcohol, in which it is readily soluble, in large, colourless, rhombic plates, m. p.  $136^\circ$  (Found: S, 49.4%). It is moderately easily soluble in cold water and very readily in organic solvents. It is reduced to  $\alpha$ -trithioacetaldehyde by warming with zinc dust and dilute hydrochloric acid.

$\alpha$ -Trithioacetaldehyde  $\beta$ -monosulphoxide crystallises from 10% alcohol in slender colourless prisms, m. p.  $93^\circ$  (Found: S, 49.4%). Its solubilities are only slightly greater than those of the  $\alpha$ -form, above. It is reduced by nascent hydrogen to  $\alpha$ -trithioacetaldehyde.

Each of the three isomeric monosulphoxides lowers the m. p. of either of the others.

*Oxidation of  $\alpha$ -Trithioacetaldehyde to a Pair of Isomeric Monosulphones.*—8.3 G. of  $\alpha$ -trithioacetaldehyde were oxidised to the monosulphoxide stage, as above, with "perhydrol." To the solution in acetic acid, aqueous caustic potash was added until the mixture was just alkaline to phenolphthalein; the total volume of the solution was then about 1200 c.c. 20 G. of magnesium sulphate were dissolved in this, and 4.9 g. of potassium permanganate, dissolved in 500 c.c. of water, added with mechanical stirring during 9 hours. The resulting reaction mixture was worked up as described for  $\beta$ -trithioacetaldehyde monosulphone. Yield of crude product, 9.5 g. By fractional crystallisation from alcohol, two isomeric products were isolated.

$\alpha$ -Trithioacetaldehyde  $\alpha$ -monosulphone is sparingly soluble in water, more readily in alcohol. It crystallises in two polymorphic forms. When a hot alcoholic solution is cooled, the labile form

separates as a felted mass of colourless needles. These, on standing in contact with the solvent for 24 hours at the ordinary temperature, dissolve, and the stable form separates as large, colourless, rhombic crystals. Both forms melt at  $157.5^{\circ}$ , transformation into the stable form occurring before melting (Found : S, 45.3%).

$\alpha$ -Trithioacetaldehyde  $\beta$ -monosulphone crystallises from alcohol, in which it is appreciably more soluble than the  $\alpha$ -monosulphone, in slender colourless prisms, m. p.  $115-116^{\circ}$  (Found : S, 45.1%).

These two isomerides are stable towards reducing agents in the same way as is  $\beta$ -trithioacetaldehyde monosulphone. They do not undergo stereoisomeric inversion under the influence of hydrogen iodide, iodine or acetyl chloride. The  $\alpha$ -monosulphone corresponds to the  $\alpha$ -monosulphoxide, since if the latter compound is oxidised with the appropriate amount of neutral permanganate, the  $\alpha$ -monosulphone is obtained alone in practically quantitative yield.

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OXFORD.

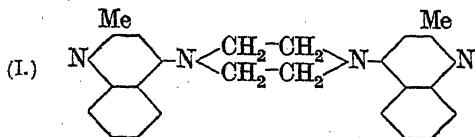
[Received, April 12th, 1930.]

## CLXXVI.—Attempts to find New Antimalarials. Part V. Some Piperidino- and Piperazino-derivatives of Quinoline.

By WILLIAM OGILVIE KERMACK and JAMES FERGUS SMITH.

4-CHLORO-2-METHYLQUINOLINE and its derivatives, which are readily obtained by the treatment with phosphoryl chloride and phosphorus pentachloride, of the corresponding 4-hydroxy-2-methylquinolines, prepared according to the method of Conrad and Limpach (*Ber.*, 1887, 20, 947) by the condensation of ethyl acetoacetate with the requisite derivatives of aniline, condense readily with various primary and secondary amines. For instance, 4-piperidino-2-methylquinoline and 4-piperidino-6-methoxy-2-methylquinoline were obtained from piperidine and 4-chloro-2-methylquinoline and 4-chloro-6-methoxy-2-methylquinoline, respectively, at  $180^{\circ}$ .

When 4-chloro-2-methylquinoline was heated at  $140^{\circ}$  with a considerable excess of piperazine hexahydrate for 2—3 hours, a white solid separated, from which 4-piperazino-2-methylquinoline was



isolated, besides a small quantity of 1:4-di-2'-methyl-4'-quinolyl-piperazine (I). When relatively less piperazine was used, a corre-



spondingly larger quantity of (I) was formed. Under similar conditions 4-chloro-6-methoxy-2-methylquinoline condensed with piperazine hydrate with the formation of 4-*piperazino*-6-methoxy-2-methylquinoline and 1 : 4-di-6'-methoxy-2'-methyl-4'-quinolylpiperazine.

The preparation of mono-*N*-substituted derivatives of piperazine usually presents considerable difficulty, and, with the simpler reactive halides, the disubstituted compound is usually obtained exclusively, or in preponderating amount (compare Moore, Boyle, and Thorn, J., 1929, 39). *p*-Chloronitrobenzene is said to yield the monosubstituted derivative readily; it is therefore of some interest that 4-chloro-2-methylquinoline and its derivatives can without difficulty be made to react with piperazine so as to yield monosubstituted products.

Certain of the above compounds have been tested in respect of their antimalarial action, and the results of these biological experiments will be published elsewhere. As in other papers of this series, the numbers, given in parentheses, after certain compounds are to facilitate reference to the biological tests.

#### EXPERIMENTAL.

4-*Piperidino*-2-methylquinoline (Km. 10).—Equimolecular quantities of piperidine (2.5 g.) and 4-chloro-2-methylquinoline (5.3 g.) were heated together at 180° under reflux for 3—4 hours. The purple solid which separated was extracted with dilute hydrochloric acid (3%), and the solution made alkaline with caustic soda. The dark red oil which separated was subjected to steam distillation to remove any excess of piperidine or chloroquinoline. The residue was dissolved in ether, dried over potassium carbonate, and recovered as a dark oil. This, on distillation in a vacuum, gave a somewhat viscous, light yellow oil, b. p. 207°/12 mm., which would not crystallise. The *picrate*, obtained by means of a cold saturated solution of picric acid in benzene, crystallised from alcohol in yellow needles, m. p. 182° (Found : N, 15.4.  $C_{15}H_{13}N_2 \cdot C_6H_3O_7N_3$  requires N, 15.4%).

The *chloroaurate*, obtained by mixing a solution of the hydrochloride, containing an excess of hydrochloric acid, with an aqueous solution of gold chloride, separated as a yellow-brown precipitate, insoluble in hot water, but easily soluble in alcohol, from which it crystallised in dark red, almost rectangular, rhombic plates, m. p. 174° (Found : Cl, 24.9.  $C_{15}H_{13}N_2 \cdot AuCl_4$  requires Cl, 25.1%).

4-*Piperidino*-2-methylquinoline is fairly readily soluble in acids, although concentrated nitric acid, when added to a solution of the hydrochloride, precipitates yellow needles, m. p. 192° (decomp.), presumably the nitrate, which is sparingly soluble in cold, and rather

more soluble in hot water. The hydrochloride could not be obtained as a solid by passing dry hydrogen chloride into a benzene solution of the base. The base is somewhat soluble in most organic solvents, but is sparingly soluble in cold water. Its solution in concentrated sulphuric acid exhibits a very faint bluish fluorescence when illuminated by the arc lamp. Very little darkening of the solution is observed on warming (compare the behaviour of the methoxy-derivative).

**4-Piperidino-6-methoxy-2-methylquinoline**(Km. 12).—When equimolecular quantities of 4-chloro-6-methoxy-2-methylquinoline (6.2 g.) and piperidine (2.5 g.) were heated together under the conditions adopted in the preparation of 4-piperidino-2-methylquinoline, and the purple solid formed was extracted and purified as above, a clear yellow, viscous oil was finally obtained, b. p.  $220^{\circ}/12$  mm. The base, which could not be induced to crystallise, exhibited a strong greenish fluorescence, and in its properties closely resembled 4-piperidino-2-methylquinoline. With concentrated sulphuric acid, however, it gave a strong blue fluorescence which disappeared on dilution. On warming, the solution in concentrated acid developed an orange-brown colour, the blue fluorescence becoming less marked. The *picrate*, obtained as before, crystallised from alcohol in clusters of long yellow prisms, m. p.  $191^{\circ}$  (Found: N, 14.2.  $C_{16}H_{20}ON_2, C_6H_3O_7N_3$  requires N, 14.4%).

The *chloroaurate*, obtained as above, crystallised from alcohol, in which it was readily soluble, in red rhombic plates, m. p.  $156^{\circ}$  (Found: Cl, 24.1.  $C_{16}H_{27}ON_2AuCl_4$  requires Cl, 23.8%).

**4-Piperazino-2-methylquinoline**(Km. 13).—4-Chloro-2-methylquinoline and a large excess of piperazine hexahydrate (15 g.) were heated under reflux for 3–4 hours in an oil-bath at  $140^{\circ}$ . The white solid which separated was extracted with dilute hydrochloric acid (3%), and the solution filtered, leaving behind a small quantity of the white hydrochloride of the corresponding diquinolylpiperazine. The filtrate, when made alkaline with caustic soda, deposited a yellow oil, which slowly crystallised. On recrystallisation from hot water (in which solvent there is a marked tendency to supersaturation), large, yellow-brown, rhombic plates of the *hydrate* were obtained, m. p.  $60^{\circ}$ . These, on drying in a desiccator, lost 24.4% of their weight, corresponding to four molecules of water of crystallisation (24.1%), and yielded the anhydrous *base*, m. p.  $103^{\circ}$  (Found: C, 74.2; H, 7.5; N, 18.3.  $C_{14}H_{17}N_3$  requires C, 74.0; H, 7.5; N, 18.5%).

This compound is very soluble in alcohol, in dilute mineral, and acetic acids, soluble in ether, but very slightly soluble in benzene and in cold water; it dissolves quite readily, however, in hot water. When treated with concentrated sulphuric acid in the cold, the base

dissolves only with difficulty, yielding a clear solution; this exhibits in the arc lamp a very faint blue fluorescence which disappears on dilution. Neither the solution in concentrated sulphuric acid nor that in concentrated nitric acid exhibits any characteristic colour changes on warming (compare the methoxy-derivative).

4-Piperazino-6-methoxy-2-methylquinoline (Km. 9).—4-Chloro-6-methoxy-2-methylquinoline (5 g.) was treated with piperazine hydrate (15 g.) under the same conditions as recorded in the preparation of 4-piperazino-2-methylquinoline. In this case, none of the corresponding diquinolylpiperazine was formed, the compound being obtained in a very pure form by diluting the condensation product with 3—4 times its volume of water and allowing the hot solution to stand; crystals of the *hydrate* soon separated as pink pyramids which, after recrystallisation from hot water, melted at 55°. These crystals, when dried in a desiccator, lost 17.9% of their weight, corresponding to three molecules of water of crystallisation (17.4%), and yielded the anhydrous *base*, m. p. 113° (Found: C, 69.7; H, 7.5; N, 16.0.  $C_{15}H_{13}ON_3$  requires C, 70.0; H, 7.4; N, 16.3%).

This compound resembles 4-piperazino-2-methylquinoline in solubility. Its solution in cold concentrated sulphuric acid, however, exhibits a very strong greenish-blue fluorescence which disappears on dilution. When the concentrated acid solution is warmed, a reddish-brown colour develops and the fluorescence, although less marked, is retained. When treated with hot concentrated nitric acid, this compound develops a red colour.

4'-Acetyl-4-piperazino-2-methylquinoline.—4-Piperazino-2-methylquinoline was heated with acetic anhydride for 2—3 hours on the water-bath, the product warmed with water, and the solution made alkaline with caustic soda. The oily base obtained, which solidified, crystallised from hot water in large, brown, rhombic plates of the *hydrate*, m. p. 70°. When dried in a desiccator, these crystals lost 16.9% of their weight, equivalent to three molecules of water of hydration (16.7%), and yielded the anhydrous base, m. p. 122°.

This acetyl derivative resembles the parent base in solubility and in exhibiting a very faint blue fluorescence in concentrated sulphuric acid solution, by the arc light. In addition, its alcoholic solution exhibits a slight greenish fluorescence.

4'-Acetyl-4-piperazino-6-methoxy-2-methylquinoline (Km. 11).—This compound was prepared in a similar manner to the preceding one. The *hydrate* was obtained from hot water in light brown needles, m. p. 86°, which, when dried in a desiccator, lost 10.9% of their weight, equivalent to two molecules of water of crystallisation (10.7%), and yielded the anhydrous base, m. p. 154°.

Here again, the properties of this acetyl derivative resemble closely

those of the parent base. The distinctive colour reactions shown by 4-piperazino-6-methoxy-2-methylquinoline when warmed with concentrated nitric or sulphuric acid, as well as the fluorescences exhibited, were slightly more marked in this case. In addition, its solution in alcohol exhibits a slight greenish fluorescence.

1 : 4-*Di-2'-methyl-4'-quinolylpiperazine* (Km. 14).—4-Chloro-2-methylquinoline (3.5 g.) was condensed with piperazine hydrate (2 g.) under the same conditions as those adopted in the preparation of the monoquinolylpiperazines. The white solid which had separated after 2—3 hours was treated with cold hydrochloric acid (3%), which removed any unchanged materials, and was then dissolved in a large quantity of boiling water; when this solution was made alkaline with sodium hydroxide, the *base* was obtained as a voluminous white precipitate. It was practically insoluble in most organic solvents, but crystallised from hot pyridine in white rhombohedra, m. p. 314° (Found: C, 78.1; H, 6.7.  $C_{24}H_{24}N_4$  requires C, 78.3; H, 6.5%).

This compound is fairly readily soluble in acetic and lactic acids, but forms sparingly soluble salts with dilute hydrochloric, nitric and sulphuric acids. It dissolves, however, in concentrated nitric acid to give a light yellow solution, which darkens only slightly on warming (compare the methoxy-derivative). With concentrated sulphuric acid, it yields a clear solution which exhibits a very faint violet fluorescence in the arc light. When warmed, this solution rapidly turns green, changing to greenish-brown and finally dirty brown.

1 : 4-*Di-6'-methoxy-2'-methyl-4'-quinolylpiperazine* (Km. 15).—This compound was obtained when 4-piperazino-6-methoxy-2-methylquinoline (2.5 g.) and 4-chloro-6-methoxy-2-methylquinoline (2 g.) were heated together at 140° for 2—3 hours, or when 4-chloro-6-methoxy-2-methylquinoline (4 g.) and piperazine hydrate (2 g.) were heated under the same conditions as in the preparation of the last compound. In either case, the *base* was obtained as a white solid when a hot aqueous solution of the buff-coloured hydrochloride was made alkaline with caustic soda, the hydrochloride being readily isolated from the reaction mixture on account of its insolubility. The *base* crystallised from hot pyridine in pink rhombohedra, m. p. 286° (Found: C, 72.5; H, 6.5.  $C_{26}H_{28}O_2N_4$  requires C, 72.9; H, 6.5%).

In its sparing solubility in most solvents it resembles very closely 1 : 4-di-2'-methyl-4'-quinolylpiperazine, already described. When its solution in concentrated nitric acid is warmed, however, a dark red coloration quickly develops. Its pale yellow solution in concentrated sulphuric acid exhibits a strong green fluorescence which

disappears on warming, the solution becoming successively pale violet, dark violet, and finally reddish-purple.

The authors desire to express their thanks to the Advisory Council of the Department of Scientific and Industrial Research and to the Trustees of the Carnegie Trust for the Universities of Scotland for a grant and a Research Scholarship, respectively, to one of them (J. F. S.), which have enabled this research to be carried out.

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## CLXXVII.—*The Passivity of Metals. Part V. The Potential-Time Curves of Some Iron Alloys.*

By L. C. BANNISTER and ULICK R. EVANS.

PREVIOUS work (Evans and Stockdale, J., 1929, 2651) having shown that those oxide films which give the best protection are the most difficult to remove, it seemed necessary to develop a method of studying the character of such films whilst they were still adhering to the metal. The most promising scheme was based on an examination of time-potential curves similar to those obtained by May (*J. Inst. Metals*, 1928, 40, 141), by McAulay and Bastow (J., 1929, 85), by W. J. Müller and Konopicky (*Monatsh.*, 1929, 52, 463), and by Speller (private communication). Such curves have already been studied by one of us (Evans, J., 1929, 92), but the method employed allowed the liquid to have access to the cut edges of the vertical specimens, causing complications due to shearing stresses and exposure of the interior layers, which in rolled metals may differ physically and chemically from the face; furthermore, the inconveniently rapid movement of the potential made it difficult to obtain early values.

A new method has now been worked out in which specimens are placed horizontally and arranged so that their edges do not come into contact with the liquids. The potential movement is here comparatively slow. An improved method of measuring the potential has also been adopted, and in this way a study has been made of the behaviour of different varieties of iron with or without carbon, copper, nickel, chromium, and molybdenum; a few experiments have also been carried out with aluminium.

### EXPERIMENTAL.

*Materials.*—The iron E 28 and steel H 28 were kindly presented by Dr. W. H. Hatfield and the steels K 1 and K 2 by Mr. Taylerson, of

Pittsburgh, Pa.; K 1 is a typical American copper steel. In considering the analyses given below, it should be remembered that practically all commercial irons contain copper, and that amounts below 0.05% are usually recorded in routine analysis as "traces."

	E 28.	H 28.	K 1.	K 2.
Carbon .....	0.03	0.26	0.055	0.11
Silicon .....	Trace	0.15	0.010	0.010
Sulphur .....	0.005	0.014	0.052	0.037
Phosphorus .....	0.020	0.018	0.078	0.060
Manganese .....	0.04	0.57	0.31	0.51
Copper .....	Nil	0.045	0.187	0.052
Thickness (mm.) .....	0.34	0.32	0.86	0.86

In addition a sample of "Staybrite" steel, an austenitic alloy with 18% of chromium and 8% of nickel, was the gift of Dr. W. H. Hatfield, whilst Mr. J. H. G. Monypenny very kindly provided specimens of the following alloys :

	Cutlery "stainless steel."	"Stainless iron."	"Two- score."	"Anka."	"B.B.4K."
Carbon .....	0.27	0.09	0.12	0.12	0.13
Silicon .....	0.19	0.22	0.40	0.24	0.54
Sulphur .....	0.045	0.033	0.032	0.033	0.052
Manganese ...	0.17	0.19	0.82	0.18	0.13
Chromium ...	13.2	13.6	17.4	15.6	17.2
Nickel .....	0.20	0.36	2.15	10.5	10.1
Molybdenum	—	—	—	—	3.42
Tempering temperature	750°	700°	650°	—	—
Thickness (mm.) .....	2.21	1.66	1.66	2.18	1.19

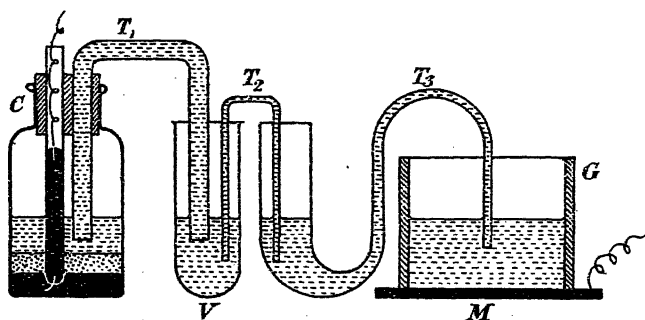
Of these, "Anka" and "B.B.4K" had been heated to 1000—1050° and air-cooled; the structure was wholly austenitic. The others were "hardenable" steels, softened, after rolling, by tempering at the temperature indicated; these exhibited a duplex structure, with carbide as minute particles distributed in the ferrite.

The aluminium was of two types: (a) electro-refined sheet (soft) with 0.013% of silicon, 0.012% of iron, 0.014% of copper, and 0.004% of titanium, kindly supplied by Mr. E. H. Dix of the Aluminium Company of America, and (b) some soft sheet of British origin containing 0.33% of silicon and 0.40% of iron.

*Procedure.*—The materials E 28 and H 28 were ground with French emery paper No. 1. For the harder materials, grinding on a coarse wheel was necessary. In some cases, this was followed by grinding with successively finer grades of emery, ending with French No. 1; this will be called "sequence-finish." After abrasion they were degreased with carbon tetrachloride. A glass cylinder of 3.5 cm.

diameter and 3 cm. height ( $G$ , Fig. 1), ground flat at the bottom, was cemented on to the metal ( $M$ ) by means of nitrocellulose solution, and the whole was exposed to air for a week, with protection from dust and moisture. The calomel electrode  $C$  and connecting tubes  $T_1$ ,  $T_2$ , and  $T_3$  were then placed in position. The whole was introduced into an outer glass vessel surrounded with a water jacket, itself heavily lagged. This vessel contained a dish of 3*N*-sodium hydroxide—the concentration shown by Mitsukuri (*Sci. Rep. Tōhoku Imp. Univ.*, 1929, 18, 245) to be the most efficient in absorbing traces of acid fumes. In the potassium chloride experiments, all the tubes and vessels contained  $M/10$ -potassium chloride (that in  $C$  and  $T_1$  being saturated with calomel). In the potassium chromate experiments,  $T_2$ ,  $T_3$ , and  $G$  contained  $M/10$ -potassium chromate, whilst saturated potassium chloride was used in  $V$ ; some care was necessary to exclude traces of chloride from  $G$ , or low values were obtained.

FIG. 1.

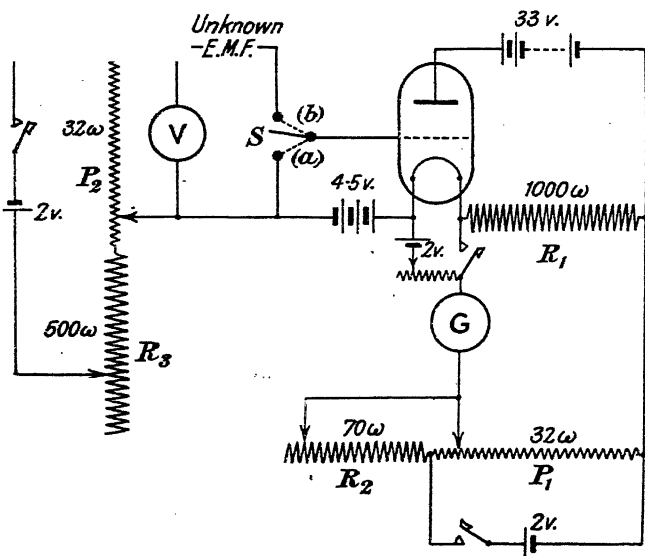


All the tubes and the vessel  $V$  were filled before shutting up the outer vessel, but the liquid was only introduced into  $G$  through a vertical tube at the start of the experiment proper; the depth of the liquid was 1.8 cm. and the bottom of the tubulus was about 1 cm. above the metal.

The arrangement for measuring the potential is shown in Fig. 2. It depends on the principle employed by May (*loc. cit.*), modified to give increased sensitivity; the valve employed was Mullard No. PM 252. When the switch  $S$  is in position ( $a$ ), the grid bias is 4.5 volts, and a small current flows through the anode circuit and causes a fall of potential over the resistance  $R_1$ , producing a deflexion to right or left on the detector  $G$ ; the potentiometer resistance  $P_1$  is adjusted until this deflexion vanishes. A movement of the switch  $S$  into position ( $b$ ) brings the *E.M.F.* to be measured into the grid circuit, and by altering the grid bias, causes again a deflexion on  $G$ . The potentiometer resistance  $P_2$  is then moved until the deflexion on

$G$  is again zero, which will clearly be the case when the potential drop on  $P_2$  is exactly equal and opposite to the  $E.M.F.$  to be measured; this value can then be read directly on the voltmeter  $V$ . Practically no current passes through the experimental cell, even when the apparatus is out of adjustment. The use of the shunt resistance  $R_2$  and the series resistance  $R_3$  was necessary to obtain the required fine adjustment.

FIG. 2.



A list of experiments performed is shown in Table I, together with the general form of the curves, and the value of the (hydrogen scale) potential after 2 hours (it was usually fairly constant after this time); the temperature was  $15^\circ$ . Some of the curves are shown graphically in Figs. 3 and 4. The time scale of the two diagrams is different, and on Fig. 4 it has been necessary to omit some of the early points, but these all lie on the curves. The potentials are expressed on the normal hydrogen scale, and the times measured from the moment of introduction of liquid. The measurements were usually continued for 3 hours. Table I shows that after 2 hours the values reached in duplicate experiments were generally much the same, but there was often rather more discrepancy between the earlier parts of the curves, where the potential was fluctuating in an irregular manner.

*The Significance of the Potential of Film-covered Metal.*—The potential of a metal covered with a discontinuous oxide film will in general be intermediate between the values given by uncoated metal and by solid oxide; the more porous the film is, the nearer will the



TABLE I.

Expt. No.	Material.	Treatment.	Liquid.	Nature of curve.	Potential.
0	Iron E 28	Coarse wheel alone	M/10-KCl	Falling	-0.410
1, 2	"	French emery No. 1	"	"	-0.405
3, 4	Steel H 28	"	"	"	-0.410
5, 6	Iron E 28	"	"	"	-0.420
7	Steel H 28	"	{ M/10-KCl + M/10-K <sub>2</sub> CrO <sub>4</sub>	"	-0.420
8	Iron E 28	"	"	"	-0.280
9, 10	Steel H 28	"	M/10 <sup>2</sup> -K <sub>2</sub> CrO <sub>4</sub>	Initial rise	-0.240
11, 12	Steel K 2	Sequence *	"	"	-0.248
13, 14, 15	" Copper steel " K 1	"	M/10-KCl	Falling	+0.310
16, 17	" Stainless iron "	Coarse wheel alone	"	"	+0.293
18, 19	Cutlery " stainless steel "	"	"	"	-0.470
20, 21	" " "	Coarse wheel, then nitric acid (d 1.20)	"	"	-0.480
22, 23	" Two-score "	Coarse wheel alone	"	"	-0.450
24, 25	"	Sequence *	"	"	-0.480
26	" Anka "	Coarse wheel alone	"	Initial fall	-0.155
27, 28	" B.E.A.K "	"	"	"	-0.173
29	" Staybrite "	"	"	"	-0.103
30	"	Wire-brushed	"	"	-0.205
31	"	As 30, but oxide removed	"	"	-0.190
32	"	Wire-brushed, then nitric acid (d 1.20)	"	"	-0.218
33	"	Sequence *	"	Nearly level	-0.073
34	"	Sequence, * annealed	"	{ Initial irregularity then nearly level	-0.118
35	"	As 34, but oxide removed	"	{ Slight initial fall then level	+0.170
36	"	Sequence, * then nitric acid (d 1.20)	"	{ Initial irregularity, then level	+0.028
37	"	Highly polished	"	Initial fall	+0.123
38	Aluminium (a)	Wire-brushed	"	Initial rise	+0.106
39	"	French emery No. 1	"	Falling	-0.023
40, 41	"	Cold-rolled	"	Initial fall	-0.083
42, 43	Aluminium (b)	French emery No. 1	"	"	-0.085
		"	"	"	+0.128
		"	"	"	-0.172
		"	"	"	+0.078
		"	"	"	+0.163
		"	"	Gradual rise	+0.510
		"	"	Initial rise	-0.452
		"	"	Nearly level	-0.435
		"	"	"	-0.424
		"	"	"	-0.445
		"	"	Very gradual rise	-0.425
		"	"	Very gradual rise	-0.425

\* "Sequence" indicates abrasion on the coarse wheel, followed by grinding with emery of diminishing coarseness, ending with French No. 1.

potential be to the value for uncoated metal (W. J. Müller, *Monatsh.*, 1929, 52, 221; Evans, J., 1929, 104). With a highly porous film,

FIG. 3.

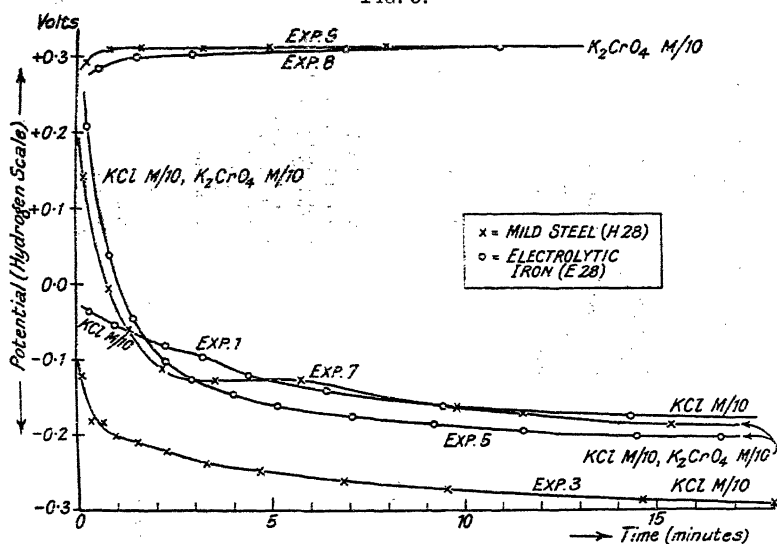
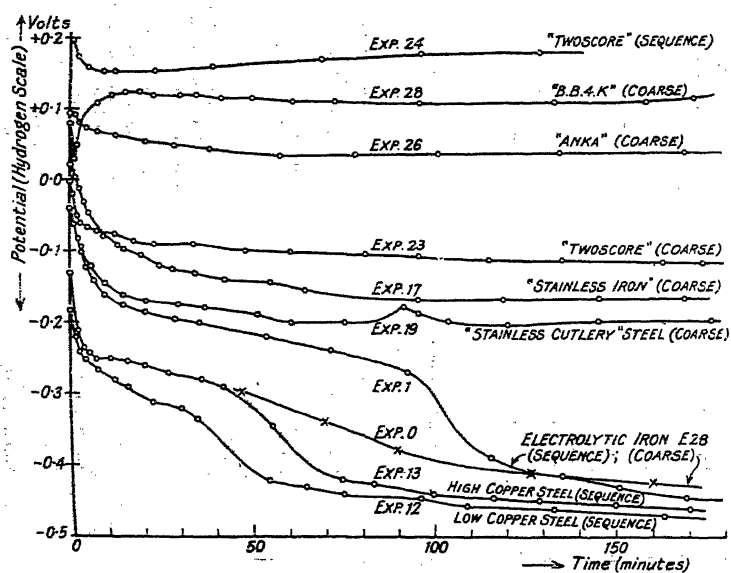


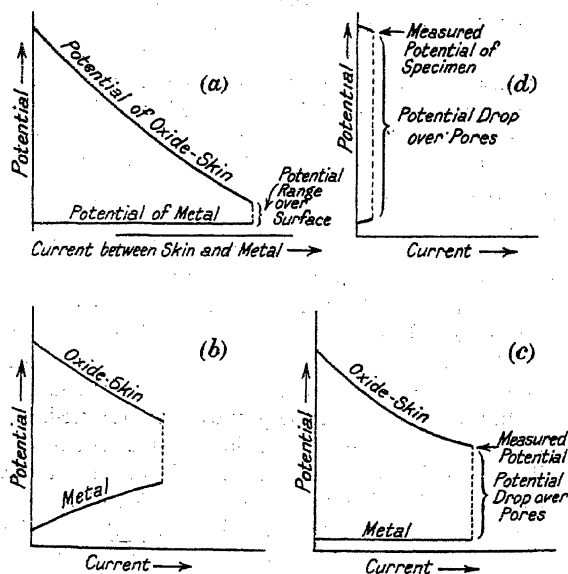
FIG. 4.



the resistance of the short-circuited cell, metal | electrolyte | oxide, will generally be low, and the minute local currents that pass between

the oxide skin as cathode and any accessible metal as anode will be regulated by polarisation, and particularly by the amount of dissolved oxygen (depolariser) reaching the oxide skin. In general, we may expect the potential at the oxide (cathodic) surface to descend with current flowing until it nearly meets the anodic potential, as indicated in Fig. 5(a); the slight difference of potential remaining when the "rest-current" is passing is that needed to force this weak current through the small ohmic resistance of the circuit. In some cases the anode potential may rise to meet the cathodic potential, as in Fig. 5(b).

FIG. 5.



In order to obtain some idea as to whether this is a true picture of the process, an experiment was performed in which, instead of a porous oxide film, a coat of a "noble" metal pierced by a hole was used. A sheet of iron was ground, and covered with a pierced sheet of copper, which was insulated from it with paraffin wax; the whole was covered with  $M/10$ -potassium chloride. The potentials were measured against two calomel electrodes, the tips of the two tubuli being almost in contact with the two metallic surfaces. Whilst electrically insulated, the two metals showed very different potentials (+ 0.083 volt for copper and - 0.102 volt for iron); but when put into electrical contact, the copper potential fell whilst the iron potential rose, so that the whole bi-metallic specimen became

practically equipotential, the value being  $+0.048$  volt at the copper surface and  $+0.043$  volt at the iron. Other experiments confirmed this; the time needed for the mutual approach of the two values varied considerably with the conditions.

The value of the "compromise" potential reached by a bi-metallic system depends on the relative areas of the two metals. An iron sheet was inserted vertically in  $M/10$ -potassium chloride, and the tip of a narrow copper strip was allowed just to touch the liquid. The potential of the iron was  $-0.317$  volt and of the copper  $+0.098$  volt; they were joined, and the copper potential at once fell to  $-0.322$  volt, the value then shown also by the iron. Here the anodic area is large compared with the cathodic area, and only the cathodic polarisation is important. The conditions were then reversed by using a copper sheet and the tip of a narrow iron strip. Here the potentials were  $-0.217$  volt for the iron and  $+0.118$  volt for the copper before the connexion; after short-circuiting, the values moved to  $-0.092$  volt for the iron and  $+0.048$  volt for the copper, whilst 6 minutes later the values were respectively  $-0.057$  and  $-0.037$  volt—a difference of only 20 millivolts.

It has often been assumed that the potential exhibited by a bi-metallic specimen is that of the more reactive metal present; but this is only true provided that, in the short-circuited cell produced, (a) the cathodic greatly exceeds the anodic polarisation, and (b) the resistance is negligible; under such conditions, the cathodic potential will drop almost to the original anodic value. When the anodic area is very small, the rise in the anode potential, as measured, is quite considerable; it is uncertain whether this measured rise is due to a *real* anodic polarisation or to the fact that, when the anodic area is a mere point, a considerable fraction of the ohmic resistance of the circuit falls between the tubulus and the metal, thus causing an "apparent anodic polarisation." In either case the "compromise" potential is not equal to the unpolarised potential of the reactive constituent.

Previous work (Evans, *J. Inst. Metals*, 1928, 40, 121) has shown that when the zinc layer of zinc-covered iron is removed gradually with acid, the potential rises as the area of exposed iron increases; any value between the potential of zinc and the potential of iron is possible for the system. Similarly, when a metal is covered with a porous oxide film, it may show *any* value between the potentials of the clean metal and the solid oxide. If the oxide film is highly discontinuous, the potential measured will be practically that of film-free metal [Fig. 5(a)]. If the cracks in the skin are extremely small, the measured potential will be higher; this is pictured in Fig. 5(b) on the assumption that a true anodic polarisation contri-

butes to the rise in the compromise value, and in Fig. 5(c) on the assumption that the elevation in the measured potential is simply due to the high resistance imposed by the narrowness of the pores. If, when this stage has been reached, the breakdown extends from the original weak points, the potential will fall, first rapidly and then more slowly, as the conditions approach the limiting case pictured in Fig. 5(a); the shutting off of oxygen by secondary corrosion product (e.g., rust) will contribute to the fall. Conversely, if repairing influences prevail, causing the pores to become narrower or less frequent, or rendering the film thicker, the measured potential will rise. The limiting case where the pores vanish and the potential becomes equal to that of a "solid" oxide electrode may not often be reached in practice; Fig. 5(d) suggests the state of affairs just before the pores vanish.

The potential of the metal just after immersion is of special interest. It has been shown by independent methods (Freundlich, Patscheke, and Zocher, *Z. physikal. Chem.*, 1927, **128**, 321; **130**, 289; Evans, J., 1927, 1029) that, in dry air, oxidation of iron commences very rapidly; but since interference colours never appear, even after months, it is evident that the film must quickly become impenetrable to oxygen molecules. If therefore the solution contains nothing more penetrating than oxygen molecules, it should show the oxygen potential, at least at the moment of immersion. Experiments 1 and 3 (Fig. 3) show clearly that, on chromium-free iron, even the initial potential is a comparatively low one. Evidently, the solution contains some constituents more penetrating than oxygen molecules; in the chloride solution, these are no doubt the chlorine ions, which will enter pores in the skin inaccessible to oxygen, and allow anodic attack on the metallic iron, generating ferrous chloride, the corresponding amount of potassium hydroxide being formed at the cathodic (oxide) surface outside. The ferrous chloride and potassium hydroxide will interact to give hydroxides of iron. If the pores are very small (approaching molecular size), the iron hydroxide will be produced at the mouth of the pores practically in contact with the iron, and may easily help to heal the defects in the original skin; thus, in some of the iron alloys where the potential is high at first, the potential actually rises (see Fig. 4, Expt. 28). Where the cracks are considerable at first, however, the iron hydroxide will generally be precipitated at a sensible distance as a loose membrane, which will not be protective; indeed, it may actually stimulate the attack by excluding oxygen. Thus in most of the irons and steels which show low initial potentials, the potential drops with the time (see Fig. 3, Expts. 1 and 3).

It will be noticed that chromium-free iron and steel, which show

falling potentials in chloride solution; show rising potentials in chromate solution (Expts. 8 and 9); here the most penetrating anion present will be the hydroxyl ion, and any anodic attack must lead to the production of ferrous hydroxide, which will be oxidised immediately to ferric hydroxide. Thus a sparingly soluble substance is formed actually in contact with the metal, which will tend to repair the damage, however extensive it may be at the moment of immersion. This explains the rise of potential with time. If chlorides are present as well as chromates (Expts. 5 and 7), the initial potential is much the same as with chromate alone, but it falls with time, instead of rising, soon dropping to a value similar to that given by chloride solution free from chromate. But, whereas a second fall occurs after about an hour in pure chloride solution, this is prevented by the presence of chromates, so that a higher final value is obtained.

It will be noticed that the rôle assigned to chromate, and also to dissolved oxygen, is not to act directly on the exposed metal; it is highly unlikely that either type of molecule could enter pores inaccessible to gaseous oxygen. Their function seems to be to act as cathodic depolarisers at the external surface of the film, thus maintaining the current and causing a flow of anions ( $\text{Cl}'$  or  $\text{OH}'$ ) into the pores, which will produce either repair or extension of the damage, according to circumstances.

*Comparison of the Curves given by Different Materials in M/10-Potassium Chloride.*—The ferrous materials may be divided into three classes :

I. Pure irons and carbon steels, with or without copper, which are rusted freely by "ordinary waters."

II. "Stainless" irons or steels, with about 13% of chromium, which are not rusted by ordinary waters.

III. High-chromium alloys, which resist many chemicals that attack Class II.

It is noteworthy that all the materials of Class I show rather low initial potentials, and the curves fall rapidly, finally reaching values below  $-0.4$  volt. Those of Class II show higher initial potentials, but fall to final values of about  $-0.2$  volt. The resistance alloys of Class III show distinctly higher values, and, in spite of some irregularities in the early stages—doubtless due to local breakdown and subsequent repair—maintain these well. It would seem that, on alloys rich in chromium, the skin formed by the direct action of air can protect the material from the moment it enters the liquid. A comparison between Expts. 26 and 27–28 seems to suggest that molybdenum further improves the quality of the skin, although the two alloys involved have not quite the same chromium content; this accords with measurements of corrosion velocity by Rohn

(*Z. Metallk.*, 1926, 18, 387) and Endo (*Sci. Rep. Tōhoku Imp. Univ.*, 1928, 17, I, 1251).

It was noticed that, in general, those steels which attained a final value above about 0.0 volt gave no rust at the end of 3 hours, whilst those which showed negative potentials produced rust; the "stainless" steels with potentials about -0.2 volt yielded far less rust than the chromium-free steels with potentials about -0.4 volt.

Expts. 12 and 13 (Fig. 4) show that the copper steel (K 1) gives the same type of curve as the ordinary carbon steel low in copper, and although the values in the middle stages appear to be somewhat higher, the final values are about the same. Two comparative experiments with K 1 and K 2 steels (respectively high and low in copper) yielded the same potential after one week; at this time, even removal of the rust and renewal of the liquid only produced a temporary rise in the potential, which at once began to fall again. This accords with the general belief that copper does not directly increase the resistance of steel towards chloride solutions under "immersed" conditions. Copper steels do not belong to the same class as chromium steels, and are not to be regarded as non-rusting or even slow-rusting materials; it is probable that the difference of behaviour of high-copper and low-copper steels shown in atmospheric tests in America (*Proc. Amer. Soc. Test. Mat.*, 1928, 28, I, 151) is due to secondary changes in the rust after its formation, or to redeposition of copper, as indicated by the work of Carius and Schulz (*Mitt. aus dem Forschungs-Inst. der Vereinigte Stahlwerke A. G.*, 1929, 1, 177).

All the materials of Class I show (a) an initial rapid drop, followed by (b) an arrest, (c) a further drop to (d) a final constant value. The second drop (c), well shown in Expts. 1, 12, and 13 (Fig. 4), was perhaps due to the formation at this stage of a definite precipitate of ferric hydroxide which settles on the metal, and definitely shuts out oxygen from certain parts (in the early stages, there is only a colloidal suspension).

The effect of a second phase in favouring a breakdown is well brought out. The curves for steel H 28 descend more rapidly than those for electrolytic iron E 28, although the final value is not very different; this had been noticed for vertical specimens, and accords with the fact—established by laboratory and field tests—that the rusting of electrolytic iron develops less quickly than that of steel, although when once started it proceeds quite readily. Likewise, the curve for stainless iron with 0.09% of carbon stands above that for outlery stainless steel with 0.27%; this agrees with the superior resistance to corrosion of the former material. Under comparable

surface conditions, the homogeneous (austenitic) alloys yield higher curves than the duplex (hardenable) materials.

It is well known that a smooth or polished surface often remains passive where a rough surface is corroded. This is entirely in harmony with the exceptionally high value given by polished "Staybrite"—as compared with other surface treatments. Similarly, the curves yielded by electrolytic iron when prepared by abrasion on the wheel show a far more rapid descent than when prepared with French emery No. 1, whilst "Two-score" also gives lower values when prepared on the wheel alone than when afterwards finished with French emery No. 1. A comparison of Expts. 29—32 with 33—36 indicates that the latter finish develops a more resistant film than a wire-brushed surface.

A comparison of the potentials obtained with "Staybrite" after various preliminary treatments (Expts. 29—37) has some interest. Owing to the difficulty of reproducing "abrasive conditions" with this material, a 10 cm. square plate of the material was uniformly wire-brushed, and cut into four quarters, one being used in each of the four experiments 29—32; another sheet was subjected to the "sequence" of abrasive treatments, and its four quarters were used in Expts. 33—36. The curves obtained accorded generally with the known facts that (1) annealing at 500—900° lowers the resistance by causing the precipitation of a second phase, and possibly by producing a thick oxide film, which is visible, easily removed, and therefore non-protective; (2) pre-treatment with nitric acid raises the resistance of alloys of this class (Hatfield, *J. Iron Steel Inst.*, 1923, 108, 123). It should be noticed, however, that the rise of potential after nitric acid treatment, although marked for "Staybrite" both on wire-brushed and "sequence-finished" specimens, is not obtained with stainless steel finished on the coarse wheel (Expts. 18—21). The unexpectedly high value found in Expt. 35 was probably due to the fact that the thick oxide film was very easily removed from the specimen, and left a surface much smoother than the originally abraded surface.

The curves obtained with aluminium all lie very close together, in spite of differences of purity and abrasion. Although there is a slight tendency to rise in the case of the less pure variety, all the curves are nearly horizontal, in contrast with those previously obtained with specimens placed vertically, which rose rapidly (J., 1929, 106). In the case of the latter specimens, the early attack was practically confined to the water-line and cut edges, and the aluminium hydroxide was evidently precipitated at the mouth of the pores in close contact with the metal, since it gave fine rings of interference colours; any hydroxide thus precipitated would tend to heal up the weak



spots in the skin, accounting for the marked rise in potential. In the new experiments, where the water-line and cut edges are excluded, this action is evidently much slower, especially with the highly pure variety, and the potential is nearly constant.

Evidently the observed potential does not indicate the rate of corrosion; steel and aluminium give almost the same final potentials, and yet the steel is far more quickly corroded. When the shape of the potential-time curve is considered along with the "normal electrode potential" of the metal, however, the information obtained is consistent with the results of corrosion-velocity measurements and, indeed, more extensive. For steel shows at first a comparatively high value, which soon sinks to a value probably representing the potential of unprotected metal; but the potential measured for aluminium is always far above the theoretical value for this metal without a protective film, and tends to rise rather than fall with the time.

*Composition of the Protective Oxide Film.*—In previous work (Evans, J., 1927, 1020; Evans and Stockdale, J., 1929, 2651) it was shown definitely that the protective oxide film, after separation from passive iron, consisted of ferric oxide (or perhaps, in part, hydroxide) with some metallic inclusions. Bancroft, however, has written (private communication, July 3rd, 1927) that "electromotive-force measurements preclude the possibility of the film being  $\text{Fe}_2\text{O}_3$ . If one postulates that the film consists of an unstable, higher oxide, adsorbed by iron, the higher oxide would break down to  $\text{Fe}_2\text{O}_3$  as soon as you dissolve off the stabilizing iron backing." He urges that the film, as analysed, has not the composition of the film as actually present on the passive iron. Similar views have been expressed by Hale (*J. Physical Chem.*, 1929, 33, 1637).

Undoubtedly, iron rendered passive by anodic treatment has at first a high potential, due to the oxygen supercharge, which may be present as an unstable higher oxide; but Smits ("Theory of Allostropy," p. 351, Longmans Green and Co., 1922) has found that, on standing, the potential sinks with a marked arrest at about  $+0.54$  volt (hydrogen scale); presumably, if the original high value is due to a higher oxide, the arrest represents ferric oxide. Since the iron is still passive during the arrest, it would seem that a higher oxide is not necessary for passivity.

However this may be, it is clear from Table I and Fig. 3 that iron rendered passive in potassium chromate never reaches the high potentials referred to by Bancroft. Indeed, higher values than this were obtained in some experiments where crystals of natural haematite or even magnetite were used instead of a metallic specimen. Not too much importance should be attached to these measure-

ments, since the crystal could not be wholly immersed, and the measurements of the hæmatite varied from end to end, possibly owing to the zonal variation of oxygen content described by Sosman and Hostetter (*Trans. Amer. Inst. Min. Met. Eng.*, 1917, **58**, 409, 434). Actually the work of these authors, and also that of Smits and Bijvoet (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 386), Pfeil (*J. Iron and Steel Inst.*, 1929, **119**, 501), and others has shown that ferric oxide is merely a member of a range of solid solutions. Numerous observations make it doubtful whether the electrode potential can be used—as claimed by Bancroft—to estimate the oxygen content of a solid phase, and the method is particularly unsatisfactory when the phase is an oxide film backed by metal, which is probably not inaccessible to the liquid. But if Bancroft is justified in accepting the potential as evidence, it would seem that the oxide present on iron rendered passive by simple exposure to chromate or air has *not* a higher oxygen content than is represented by the formula  $\text{Fe}_2\text{O}_3$ .

*Summary.*

A new method has been worked out for obtaining potential-time curves, and has been applied in a study of the behaviour of iron, iron alloys and aluminium, after various abrasive, chemical and thermal treatments, in chloride and chromate solutions. The results given correspond to the behaviour of the film, a rising potential indicating that weak points are being repaired, and a falling potential that the breakdown is extending. A high final potential indicates immunity from attack, a middle value slight rusting, and a low value profuse rusting. Treatments known to increase the resistance to attack raise the potential, and those favouring corrosion lower the potential. The character of the curves probably indicates the "liability to corrosion" rather than the velocity of corrosion when fully developed, and gives information regarding the protective character of the skin, which velocity measurements cannot afford.

We wish to acknowledge the generosity of the Salters' Institute of Industrial Chemistry which has enabled this work to be carried out. We are also indebted to Dr. W. A. Wooster for the loan of the hæmatite crystals.

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CLXXVIII.—*The Mechanism of, and Constitutional Factors controlling, the Hydrolysis of Carboxylic Esters. Part III. The Calculation of Molecular Dimensions from Hydrolytic Stability Maxima.*

By CHRISTOPHER KELK INGOLD.

AN important consequence, implicit in the results of modern work on homogeneous catalysis, is the removal, at least for catalysis by acids and bases, of the barrier between the conceptions which formerly were often applied on the one hand to catalysed reactions and on the other to reactions independent of catalysis: since the velocity of a catalysed reaction is affected by the catalyst according to the same laws as those which would apply to an ordinary reactant, it is clearly advantageous to regard the catalyst as occupying the status of an ordinary reactant, for example, in Brønsted's theory of reaction-dynamics (*Z. physikal. Chem.*, 1922, **102**, 169). On this view, a reaction becomes a catalysed reaction when, of the various ways in which the critical complex might decompose, that in which it actually decomposes leads to the formation, as one product, of a substance identical with one of the reactants. Having regard both to modern views on the dynamics of reactions in solution, and to recent work on homogeneously catalysed reactions, the formation of a critical complex between an ester group and a catalyst may, without inevitable commitment to any precise constitutional inference, justifiably be regarded as the initial process in the hydrolysis of a carboxylic ester.

Any general discussion of the factors controlling the speed of hydrolysis of an ester by a catalyst must include consideration of (a) statistical requirements, (b) polar influences, (c) steric factors, and (d) effects due to the medium.

(a) *Statistical Requirements.*—Count must be taken of statistical requirements when either the ester or the catalyst has alternative seats of reaction, but discussion will here be restricted to cases in which the existence of alternative reactions is due solely to the constitution of the ester.

The formulation of statistical effects on the relative rates of the successive stages in the hydrolysis of a polycarboxylic ester by a single catalyst at constant temperature may be effected by consideration of a compound with  $s$  ester groups so situated that the hydrolysis of each proceeds independently of the others. In general, the probability that a catalyst molecule or ion will form a complex with a particular ester group will, for constitutional reasons, be different for each ester group. Let  $v_i$  be the catalytic coefficient for the

partial reaction consisting of the hydrolysis of the  $g$ th group in the first stage of hydrolysis, and let  $k_n$  be the total catalytic coefficient for the  $n$ th stage. Then  $k_1 = \Sigma v_g$ , where the summation extends from 1 to  $s$ . In order to calculate  $k_2$ , two points must be noted; the first is that, since the fraction of the total quantity of ester which passes on to the second stage of hydrolysis through the  $g$ th first-stage product is  $v_g/\Sigma v_g$ , the contribution to  $k_2$  made by the hydrolysis of the  $h$ th ester group in this product is  $v_g v_h/\Sigma v_g$ ; the second is that the  $s$  first-stage products yield  $s(s-1)/2$  second-stage products, each of the latter being formed from two of the former. It follows that  $k_2 = 2\Sigma v_g v_h/\Sigma v_g$ , where the summations extend from 1 to  $s$  as before, except that  $h$  is excluded from identity with  $g$ . Generalising, it is seen that each of the  ${}^s C_n$  products of the  $n$ th stage of hydrolysis is formed in  $n$  ways, and that  $k_n = n\Sigma v^{(n)}/\Sigma v^{(n-1)}$ , where  $\Sigma v^{(n)}$  is the sum of all the products of  $n$  different  $v$ 's, so that, in particular  $\Sigma v^{(1)} = \Sigma v_g$  and  $\Sigma v^{(0)} = 1$ . The statistical relation between the velocities of any two stages is therefore

$$\frac{k_m}{k_n} = \frac{m \Sigma v^{(m)} \cdot \Sigma v^{(n-1)}}{n \Sigma v^{(m)} \cdot \Sigma v^{(m-1)}} \quad (1)$$

In the special case of a dicarboxylic ester, for which  $s = 2$ ,  $m = 1$ , and  $n = 2$ , equation (1) becomes

$$k_1/k_2 = (v_1 + v_1)^2/2v_1v_2 \quad (2)$$

Furthermore, if the dicarboxylic ester is symmetrically constituted, so that  $v_1 = v_2$ , this equation reduces to

$$k_1/k_2 = 2 \quad (3)$$

The application of equations (2) and (3) may be illustrated by reference to data by J. Meyer (*Z. physikal. Chem.*, 1909, **66**, 81) for the acid hydrolysis of five dicarboxylic esters (Table I).<sup>\*</sup> In the case of methyl camphorate  $v_1$  and  $v_2$  were independently determined by direct observation on the isomeric methyl hydrogen camphorates.

TABLE I.

Hydrolyte.	Temp.	$v_1 \times 10^3$ .	$v_2 \times 10^3$ .	$k_1 \times 10^3$ .	$k_2 \times 10^3$ .	$k_1/k_2$ .	$k_1/k_2$ (calc.).
Methyl succinate .....	25°	—	—	2.40	121	1.98	2.00
Ethyl succinate .....	"	—	—	2.30	121	1.90	2.00
Methyl <i>d</i> -tartrate .....	"	—	—	1.24	62	2.00	2.00
Ethyl <i>d</i> -tartrate .....	"	—	—	1.40	68	2.06	2.00
Methyl <i>d</i> -camphorate	45	1.54	3.1	1.50	6.1	24.6	25.9

Meyer was the first empirically to observe that the ratios  $k_1/k_2$  for the two-stage acid hydrolysis of symmetrical dicarboxylic esters

<sup>\*</sup> As to units, see footnote in Part I (this vol., p. 1032).

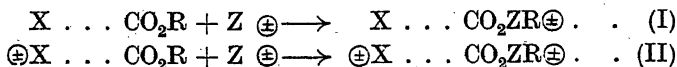
are often closely grouped about the value 2. Wegscheider (*Monatsh.*, 1915, **36**, 471) discussed the dynamical significance of this relation, noting especially that it is a peculiarity of the value 2 that the complete reaction may be represented by an integrated equation of one of the simple forms applicable to a single-stage process. Meyer's result shows clearly that, when carbomethoxyl or carbethoxyl groups are separated by a saturated chain of at least two carbon atoms, the speed of hydrolysis of each group is very nearly independent of the state of hydrolysis of the other; but this approximation would be expected to hold less exactly for malonic and oxalic esters and for completely conjugated unsaturated esters (e.g., fumaric, phthalic) owing to the intramolecular transmission of polar effects; and departures are also to be expected amongst esters of higher alcohols and compounds with endocyclic ester groups (e.g., adipodilactone) owing to spatial influences. Since later workers have usually side-stepped the accurate determination of the coefficients for the consecutive stages by regarding a more or less imperfect conformity with Wegscheider's simplified formulæ as sufficient indication that  $k_1/k_2$  is in the neighbourhood of 2, it is not yet known to what degree of approximation Meyer's result is applicable to the classes of esters mentioned. There are indications (Palomaa, *Ann. Acad. Scient. Fennicæ*, 1917, **4**, **10**, No. 16; Skrabal, *Monatsh.*, 1917, **38**, 29) that it is at least approximately applicable to oxalic and malonic esters as well as to their higher normal homologues.

Meyer noticed (*Z. physikal. Chem.*, 1909, **67**, 257) that equation (3) does not even roughly represent the alkaline hydrolysis of symmetrical dicarboxylic esters, and, indeed, this is apparent from the still earlier work of Knoblauch (*ibid.*, 1898, **26**, 96), whose coefficients for ethyl succinate bear the ratio 9.4, and of Goldschmidt and Scholz (*Ber.*, 1903, **26**, 1333), whose values for ethyl malonate give the ratio 88. Meyer remarked that this notable difference between acid and alkaline hydrolysis is probably connected with the fact that in the latter case the ester which undergoes the second stage of the reaction is an ion.

(b) *Polar Effects*.—Influences arising from the polar characteristics of the ester and catalyst may be propagated to the seat of reaction both externally (through the medium-filled space) or internally (through the linkings), and in both cases an ionic centre, if present, will dominate the situation. In the commonly employed ionic catalysts the pole itself is the reactive centre, but in esters which are also ions the pole is necessarily separated from the seat of reaction, and it is for this case, therefore, that the *propagation* of the effect of the pole requires consideration. Furthermore,

internally propagated polar effects become very small after transmission through more than two single linkings (Gane and Ingold, J., 1929, 1692, and cited references); it is therefore evident that a large class of cases must exist in which the externally propagated polar effect is for practical purposes the sole polar influence.

A basis for the calculation of the externally propagated effect is available in several well-known theoretical investigations—*e.g.*, Langevin's calculations relating to a paramagnetic gas, Debye and Hückel's treatment of the effect of interionic attraction on the activity of strong electrolytes, and especially Bjerrum's investigation of the problem presented by the strengths of polybasic acids—the common feature of all of which is the employment of Boltzmann's law. Consider two esters which are identical in all respects, except that, in some position X, the second ester has a univalent positive or negative charge not possessed by the first ester; and suppose that these esters are being hydrolysed at the same temperature by the same catalyst, which also possesses a univalent positive or negative charge. The catalytic coefficients,  $k'$  and  $k''$ , of the two reactions may for the present be assumed (see Section *d*, however) to be proportional to the mass-action rates of formation of the corresponding critical complexes :



The external molecular electric field of the first ester will render the local concentration of  $\text{Z} \oplus$  in the neighbourhood of the ester group different from its macrochemical concentration, and this will be one of the ways in which the effect exerted by polar influences on the rates of hydrolysis of esters (compare Part I, this vol., p. 1032) enters into the determination of the velocity coefficient. The external electric field of a molecule of the second ester may be regarded as equal to that due to an identically placed molecule of the first ester *plus* the radial field of a unit positive charge situated at X. This being so, Boltzmann's theorem shows that the ratio of the local concentration of  $\text{Z} \oplus$  in reaction (II) to its local concentration in reaction (I) is  $\exp(-WN/JRT)$ , where  $W$  is the work done *against the radial field alone* when  $\text{Z} \oplus$  is brought from a great distance to the focus of reaction,  $N$  is Avogadro's number, and  $J$  is the mechanical equivalent of heat. If  $r$  is the distance between the unit charge at X and the focus of reaction,  $W$  is equal to  $\pm e^2/\epsilon r$ , where  $e$  is the charge of an electron,  $\epsilon$  is the dielectric constant of the medium, and the upper or lower sign is taken according as the signs of the charges on X and Z are like or unlike. With  $e = 4.774 \times 10^{-10}$ ,  $\epsilon = 80.0$ ,  $N = 6.06 \times 10^{23}$ ,  $J = 4.19 \times 10^7$ ,  $R = 1.985$ , and  $T =$

298, the exponent has the value  $\mp 6.97 \times 10^{-8}/r$ ; and since the ratio of the local concentrations is also the ratio of the rates of formation of the critical complexes,\*

$$k'/k'' = \exp(\pm 6.97 \times 10^{-8}/r) \approx \exp(\pm 7/10^8 r) \quad (4)$$

If it is legitimate to assume that in the anion of a partly hydrolysed polycarboxylic ester the external field of each carboxylate ion can, at all distances greater than that of the nearest unhydrolysed ester group, be represented as the vector sum of that of a similarly situated carboxylic ester group and that of a superposed electron, equation (4) may be used to take count of the effect, on each stage after the first in the alkaline hydrolysis of polycarboxylic esters, of externally propagated polar fields: in these reactions the catalyst is a negative ion, and each stage of hydrolysis introduces a new negative charge into the ester molecule. Introduction of the requisite modification into equation (1) gives the relation

$$\frac{k_m}{k_n} = \frac{m \sum \{v^{(m)} \rho^{(nC_2)}\} \cdot \sum \{v^{(n-1)} \rho^{(n-1)C_2}\}}{n \sum \{v^{(n)} \rho^{(nC_2)}\} \cdot \sum \{v^{(m-1)} \rho^{(m-1)C_2}\}} \quad (5)$$

where  $\rho$  is written for  $\exp(-6.97 \times 10^{-8}/r)$ ,  $\rho^{(nC_2)}$  is the product of the  ${}_nC_2$  values of  $\rho$  corresponding with the  ${}_nC_2$  distances,  $r$ , between  $n$  ester groups taken in pairs, and brackets  $\{\}$  signify that the product of each group of  $v$ 's is to be multiplied by the corresponding  $\rho$ -product before summation. The equation for the ratio of the velocities of the stages of hydrolysis of a dicarboxylic ester is obtained from (5) by writing  $s = 2$ ,  $m = 1$ , and  $n = 2$ ; and remembering that if  $n < 2$  then  $\rho^{(nC_2)}$ , being the product of zero  $\rho$ 's, is unity:

$$\frac{k_1}{k_2} = \frac{(v_1 + v_2)^2}{2\rho v_1 v_2} = \frac{(v_1 + v_2)^2}{2v_1 v_2} \exp\left(\frac{6.97 \times 10^{-8}}{r}\right) \quad (6)$$

For the special case of a symmetrically constituted dicarboxylic ester,  $v_1 = v_2$ , and equation (6) reduces to

$$k_1/k_2 = 2/\rho = 2 \exp(6.97 \times 10^{-8}/r) \approx 2 \exp(7/10^8 r) \quad (7)$$

Table II contains all the recorded *direct* measurements of the coefficients characterising the catalysis by hydroxide ions of the consecutive stages of hydrolysis of esters of dicarboxylic acids (some measurements on hydrolysis in alkaline buffer solutions are also available and these are considered in Section *d*). The data here tabulated refer to eleven esters of seven normal dicarboxylic acids. The experimental values of  $k_1$  and  $k_2$  are given in cols. 3 and 4, and all relate to the temperature  $25^\circ$  except the two indicated by asterisks for which the temperature is  $22.7^\circ$ . Cols. 5 and 6 contain the values

\* The activity correction, which is here neglected, is considered in Section (*d*).

of  $k_1/k_2$ , which are seen to be nearly identical for methyl and ethyl esters of the same acid. Col. 7 shows the values of the distance,  $r$ , between the carboxyl groups (*i.e.*, between the charge developed on one carboxyl group and the focus of reaction at the other) as calculated from equation (7). It will be seen (a) that the distances are of the right order of magnitude (1–20 Å.U.), (b) that they place the compounds in the order of the length of the carbon chain, (c) that, having regard to the difference of method, they are in fair general agreement with the distances obtained by Gane and Ingold for the corresponding free acids (J., 1928, 1594); these distances are given in the last column for comparison.

TABLE II.

Hydrolyte.	Ref.	$k_1$ .	$k_2$ .	$k_1/k_2$ .	$k_1/k_2$ , (mean).	$r \times 10^8$ (cm.).	$r \times 10^8$ (cm.), G. & I.
Oxalate	{ methyl 4 ethyl 5	$ca. 10^6$ $ca. 10^{5.5}$	$ca. 10^2$ $ca. 10^{1.5}$	$10^4$ $10^4$	10 <sup>4</sup>	1	—
Malonate	{ methyl 3 ethyl { 2 3	170 112 136	1.84 1.27 1.46	92 88 93			
	{ 3 methyl { 6 ethyl { 1 3	20.5 26.0 13.8* 16.5	2.10 2.80 1.46* 1.59	9.8 9.4 9.4 10.4	9.7	4.4	{ 5.0 4.9†
Succinate	{ methyl 6 ethyl 3	21.6 10.0	3.16 1.63	6.8 6.1			
Glutarate	{ methyl 6 ethyl 6	1.53 1.24	0.49 0.42	3.1 2.95	2.95	17.5	17
Suberate	methyl 6	1.20	0.43	2.8			
Azelate	methyl 6				2.8	20	—
Sebacate	methyl 6						

References: (1) Knoblauch, *loc. cit.*; (2) Goldschmidt and Scholz, *loc. cit.*; (3) J. Meyer, *Z. physikal. Chem.*, 1909, **67**, 257; (4) Skrabal, *Monatsh.*, 1917, **38**, 29; (5) Skrabal and Matievic, *ibid.*, 1918, **39**, 765; (6) Skrabal and Singer, *ibid.*, 1920, **41**, 339.

† Calculated by Gane and Ingold from data by Auerbach and Smolczek.

In explanation of the approximate values for the oxalic esters, it should be stated that the only directly determined value is  $k_2$  for the methyl ester; for this the value 92 was found, but the time intervals were so short that the second figure is not significant. The same ester was also hydrolysed in carbonate buffers and from these experiments an apparent value of  $k_2$  can be calculated and compared with the directly observed value. This comparison then affords the means of estimating the true value of  $k_2$  for ethyl oxalate from the apparent values derived from similar measurements in buffers. Of the values of  $k_1$  for methyl and for ethyl oxalate, all that can be said is that they are of the order of a million and that  $k_1$  is about three times as great for the methyl as for the ethyl ester. All the other values of  $k_1$  and  $k_2$  recorded in the table represent direct determinations.

The preceding calculations neglect the internally propagated effect of the carboxylate pole, and this is expected to make the calculated



distances for oxalic and malonic esters too small; a similar error would probably affect completely conjugated unsaturated esters, such as maleic, fumaric, phthalic, and terephthalic esters, although none of these has as yet been investigated by the direct method (compare Section *d*, however); internally propagated effects should be entirely negligible in esters higher than succinic esters (Gane and Ingold, J., 1928, 1691). Furthermore, the catalytic ion has been treated as a point-charge, whereas any actual ion must become dipolarised as it approaches the charged ester molecule; this effect is expected to render the calculated distances too large throughout the series considered, and solvation, including pole-dipole association, is a form of dipolarisation which it would be necessary to envisage in any complete discussion of this disturbance. It should also be pointed out that no account has explicitly been taken of the circumstance that even in alkaline solution the electrically neutral alkyl hydrogen ester must exist as such to a minute extent, and that part of the second stage of alkaline hydrolysis of dicarboxylic esters must proceed through this form. The error due to this cause is very easy to evaluate, but it is entirely negligible in all the cases for which the writer has made the appropriate calculation; there is no point, therefore, in encumbering the equations with terms intended to eliminate this effect.

(c) *Steric Hindrance*.—It is necessary now to give attention to the circumstance that the whole of the space in the neighbourhood of a reacting centre is not *free* space in the sense envisaged by the kinetic theory, on which Boltzmann's theorem depends; in short, the effect of steric hindrance must be considered.

A basis for the discussion of this influence is furnished in Part I of this series (this vol., p. 1032) in which it was shown that velocities of hydrolysis can be represented as a simple function of polarity on the assumption that the effect of steric hindrance on the catalytic coefficients is expressible as the product of two factors *C* and *S* respectively dependent on the catalyst alone and the ester alone: if *p* is a catalytic coefficient (it was called *k<sub>p</sub>* in Part I), which is corrected in such a way as to be independent of the variability of the purely steric influences which affect in different degrees the hydrolysis of each of a series of esters by each of a series of catalysts, then the uncorrected catalytic coefficient *k* is equal to *CSp*. Reverting to reactions (I) and (II), and introducing suffixes to indicate the sign of *Z*, the preceding relation shows that

$k'_+ = C_+S'p'_+$ ,  $k''_+ = C_+S''p''_+$ ,  $k'_- = C_-S'p'_-$ ,  $k''_- = C_-S''p''_-$ ,  
and that, consequently,

$$\frac{k'_+/k''_+}{k'_-/k''_-} = \frac{p'_+/p''_+}{p'_-/p''_-} \dots \dots \dots (8)$$

From the foregoing it will be clear that the  $k$ -ratio on the left hand side of equation (4) should really be a  $p$ -ratio, wherefore, having regard to equation (8), the equation which takes account of both polar and steric influences may be written

$$\frac{k'_{-}/k'_{+}}{k''_{-}/k''_{+}} = \exp(\mp 13.94 \times 10^{-8}/r) \approx \exp(\mp 14/10^8 r) \quad (9)$$

where the upper or lower sign of the exponent is taken according as the charge on X is positive or negative in reaction (II).

In applying equation (9) to the stage-wise hydrolysis of a polycarboxylic ester, the assumption must be made that the space occupied by a carboxylate ion is equal to that filled by an undissociated carboxyl group, or at least, that it differs therefrom by a much smaller amount than that by which it differs from the space occupied by an esterified carboxyl group. Introduction of the appropriate modification into equation (5) gives the equation

$$\frac{k_{m-}/k_{n-}}{k_{m+}/k_{n+}} = \frac{\sum \{v_{-}^{(m)} \rho^{(m)C_2}\} \cdot \sum \{v_{-}^{(n-1)} \rho^{(n-1)C_2}\} \cdot \sum v_{+}^{(m)} \cdot \sum v_{+}^{(m-1)}}{\sum \{v_{-}^{(n)} \rho^{(n)C_2}\} \cdot \sum \{v_{-}^{(m-1)} \rho^{(m-1)C_2}\} \cdot \sum v_{+}^{(m)} \cdot \sum v_{+}^{(n-1)}} \quad (10)$$

For a dicarboxylic ester equation (10) reduces to the simple form

$$\frac{k_{1-}/k_{2-}}{k_{1+}/k_{2+}} = \frac{v_{1+}v_{2+}(v_{1-} + v_{2-})^2}{\rho v_{1-}v_{2-}(v_{1+} + v_{2+})^2} \quad (11)$$

The equation for a symmetrically constituted dicarboxylic ester is obtained from (11) by equating  $v$ 's of like suffix-sign. For hydrolysis by hydrogen and hydroxyl ions the equation is

$$\frac{(k_1)_{\text{OH}}/(k_2)_{\text{OH}}}{(k_1)_{\text{H}}/(k_2)_{\text{H}}} = \frac{1}{\rho} = \exp(6.97 \times 10^{-8}/r) \approx \exp(7/10^8 r) \quad (12)$$

This is the equation from which the values of  $r$  given in col. 7 of Table II were originally calculated; but since, to the accuracy with which  $(k_1)_{\text{H}}/(k_2)_{\text{H}}$  is known for the esters of oxalic acid and its normal homologues, this ratio has the value 2.0 (Palomaa), the figures are identical with those obtained from the simpler, but less theoretically defensible, equation (7).

It is not theoretically necessary that *both* the stages in the hydrolysis of a dicarboxylic ester should be investigated in order that  $r$  may be calculated: a suitable study of the second stage of hydrolysis, that is, of the hydrolysis of the acid ester only, would enable equation (9) to be directly applied. The case of acid esters is strictly comparable with that of amino-esters, and, since both forms represent the simplest types of *ionogenic* esters, they may be considered together. It can readily be shown that the curve connecting the velocity of hydrolysis of an acid ester with the hydrion concentration should,

after effects due to any buffers employed have been eliminated (Part II, this vol., p. 1039), correspond to the equation

$$v = \left\{ [H]v' \left( \frac{[H]}{H'} + \frac{H'}{[H]} \right) + K_a v'' \left( \frac{[H]}{H''} + \frac{H''}{[H]} \right) \right\} / 2(K_a + [H]) \quad (13)$$

Similarly the curve for the hydrolysis of a basic ester should be represented by the equation

$$v = \left\{ K_w v' \left( \frac{[H]}{H'} + \frac{H'}{[H]} \right) + K_b [H] v'' \left( \frac{[H]}{H''} + \frac{H''}{[H]} \right) \right\} / 2(K_w + K_b [H]) \quad (14)$$

In these equations  $K_a$  and  $K_b$  are the so-called affinity constants of the acid and base respectively, and  $K_w$  is the ionic product for water. The four quantities,  $H'$ ,  $H''$ ,  $v'$ , and  $v''$ , are constants which have to be determined from the velocity data themselves, and the significance of the first two of these is that they are the hydron concentrations at which the neutral and charged species respectively would show a velocity minimum if conversion into the other form could be prevented. Denoting the corresponding  $p_H$ 's by  $p_H'$  and  $p_H''$ , and remembering the general relation  $\log(k_{OH}/k_H) = -2p_H^* - \log K_w$ , where  $p_H^*$  is the  $p_H$  of maximal hydrolytic stability, the appropriate application of equation (9) gives

$$p_H' - p_H'' = \pm 3.03 \times 10^{-8}/r \approx \pm 3/10^8 r. \quad (15)$$

where the sign must be chosen to correspond with that of the charge developed on the ionogenic ester.

Suitable data for the evaluation of both  $p_H'$  and  $p_H''$  by the application of equations (13) and (14) are not yet available, but in the case of ethyl aminoacetate data leading to an approximate value for  $p_H''$  are on record; the figure thus obtained is not very accurate owing to the absence of data permitting the elimination of buffer effects. The value of  $p_H'$  cannot be similarly obtained, but, in accordance with the principles discussed in Part I (*loc. cit.*), it may be interpolated between the values of  $p_H^*$  for ethyl propionate and ethyl glycollate, both of which are accurately known; the probable uncertainty attending this procedure is unlikely to be much greater than that which relates to the directly measured value of  $p_H''$  in the absence of a correction for buffer effects, and is of the order of 0.1  $p_H$  unit. There is a small difference in the temperatures to which  $p_H'$  and  $p_H''$  apply, but it is negligible in the circumstances. These data are assembled in Table III, and it will be seen that the distance  $r$  for  $\text{NH}_3^+ \cdot \text{CH}_2 \cdot \text{CO}_2 \text{Et}$  is practically the same as for  $\text{CO}_2^+ \cdot \text{CH}_2 \cdot \text{CO}_2 \text{Et}$  ( $1.8 \times 10^{-8}$  cm.); owing to the structural similarity both values are probably subject to the same disturbances.

TABLE III.

Hydrolyte.	Ref.	Temp.	$p_H^*$ .	$\Delta p_H^*$ .	$r$ (cm.).
Ethyl aminoacetate .....	1	25°	5.3	1.8	$1.7 \times 10^{-8}$
Ethyl ammonium acetate ...	2	20	3.5		

References: (1) Bolin, *Z. anorg. Chem.*, 1925, **142**, 201; (2) van Dijken, *Rec. trav. chim.*, 1895, **14**, 106; Findlay and Hickmans, *J.*, 1909, **95**, 1010; Denshel and Dean, *Amer. J. Sci.*, 1912, **34**, 293; 1913, **35**, 486; Dean, *ibid.*, 1913, **35**, 605; 1914, **37**, 331; Taylor, *Medd. K. Vetenskapsakad. Nobel-inst.*, 1913, **2**, No. 34; Palomaa, *Ann. Acad. Scient. Fennice*, 1913, *A*, **4**, No. 2; 1914, *A*, **5**, No. 4; Lambie and Lewis, *J.*, 1914, **105**, 2330.

(d) *Effects due to the Medium.*—Consideration has not yet been given to possible disturbances due to the medium. The expected disturbances are of two kinds.

(1) The dielectric constant of water containing both electrolytes and non-electrolytes will only be approximately equal to that of pure water even at the considerable dilutions to which the measurements in Table II relate; the non-electrolytic solutes would tend to decrease the constant, whilst the electrolytes might decrease it or increase it according to their concentration (Debye). The consideration of this effect involves no new principle and an appropriate correction could readily be introduced if the requisite data were available.

(2) For solutions of considerable ionic strength, the relation,  $v = kC_A C_B$ , hitherto used, requires a correction which, according to Brønsted (*loc. cit.*), is represented by  $f_A f_B / f_{AB}$  in the equation  $v = kC_A C_B f_A f_B / f_{AB}$ . This equation shows that, whilst the simpler equation should be valid for the hydrolysis of neutral esters by ions, the velocity of ion-catalysed hydrolysis of ionic esters will increase or decrease with increasing ionic strength ( $\mu$ ) according as the charges on the reactants are like or unlike in sign. In the second stage of the hydrolysis of a dicarboxylic ester the charges are of like sign, and hence the velocity should increase with increasing ionic strength. In order to show that this effect is not negligible, Table IV is appended, the data in which are taken from Skrabal and Singer's published results.

TABLE IV.

Hydrolyte.	Catalyst.	Inert salt.	$\mu$ (initial).	$k$ .
$\text{NaO}_2\text{C}\cdot\text{CO}_2\text{Me}$	$\text{Na}_2\text{CO}_3$	—	0.40	1.8
		0.40 <i>N</i> -NaCl	0.80	2.1
$\text{NaO}_2\text{C}\cdot(\text{CH}_2)_2\cdot\text{CO}_2\text{Me}$	$\text{NaOH}$	—	0.004	2.8
"	"	—	0.032	3.4
"	"	—	0.040	3.9

Now, assuming for the moment that only univalent anions are under consideration, the formulæ already developed for the ratio,  $k_1/k_2$ , obtaining in the two-stage hydrolysis of a dicarboxylic ester,

show that this ratio should be independent of the nature of the catalysing anion, provided that the concentration is so low that the ionic-strength disturbance is negligible. This condition is very approximately fulfilled in the hydrolysis with sodium hydroxide for which the ionic strength is 0.01 or less; but when buffer solutions are employed the ionic strength is usually of the order 0.1—1.0. In the complete hydrolysis of a dicarboxylic ester in alkaline buffers, the first stage escapes the ionic-strength effect, but the second stage is subject to it, and thus the values of  $k_1/k_2$  obtained by the use of buffers are rendered too low. Against this must be set the circumstance that some small part of the total hydrolysis will undoubtedly be effected, not by hydroxide ions, but by the buffer anions themselves, and if these are more than univalent—and carbonate-bicarbonate buffers have usually been employed—the higher valency will create an effect tending to make  $k_1/k_2$  too large. The general conclusion must, therefore, be that little reliance can be placed on anything but the order of magnitude of this ratio when it is deduced from experiments with buffers; nevertheless, in order to complete the survey of existing relevant data, the values of the ratio, which are deduced from measurements with carbonate-bicarbonate buffers, are given in Table V for those esters which have been studied in this way. The values of  $r$  calculated from equation (7) are in the last column. When data become available for the activity coefficients of the electrolytes and the catalytic coefficients of the buffer anions, it should be possible to correct these values; in the meantime it is seen that, where comparison can be made with  $r$ -values based on direct determinations of the  $k$ -ratio, the agreement is poor to moderate. A clear illustration of the importance of the ionic-strength effect appears in the values for methyl *d*-tartrate and methyl racemate, for the hydrolysis of which carbonate-bicarbonate buffers of two concentrations have been employed; it will be noticed that when the ionic strength at the commencement of reaction is increased from about 0.05 to about 0.5, the value of  $k_1/k_2$  falls by 30%.

Finally it may be pointed out, first, that since the maleic and fumaric esters were hydrolysed by buffers of similar concentration, the error in  $r$  caused by ionic-strength effects is probably similar in both cases, and, secondly, that, although, as explained in Section (b), internally transmitted polar effects will make the  $r$ -values too small, the type of conjugation which gives rise to this result is the same for both esters, wherefore the disturbances will probably be nearly the same. Since a little further consideration readily shows that the necessary corrections, which although unknown are presumed to be nearly equal, would be represented by *factors*, and not differences, it follows that the ratio,  $r_{\text{fumaric}}/r_{\text{maleic}}$ , should be subject, certainly to

TABLE V.

Measurements in buffers.

Hydrolyte.	Ref.	$\mu$ (initial).	$k_1/k_2$ .	$r \times 10^8$ (cm.).	From Table II $r \times 10^8$ (cm.).
Methyl malonate .....	1	0.50	73	1.9	1.8
Ethyl malonate .....	1	0.50	67	2.0	1.8
Methyl succinate .....	1	0.45	4.7	8.2	4.4
Methyl maleate .....	3	0.07	67	2.0	—
Methyl fumarate .....	3	0.05	22	2.9	—
Methyl <i>d</i> -tartrate .....	2	0.55	14.7	3.5	—
Methyl <i>l</i> -tartrate .....	4	0.06	19.5	3.1	—
Methyl <i>l</i> -tartrate .....	4	0.06	20	3.0	—
Methyl racemate .....	4	0.55	14	3.6	—
Methyl <i>l</i> -tartrate .....	4	0.06	20	3.0	—
Methyl mesotartrate ...	4	0.06	28	2.7	—

References : (1) Skrabal and Singer (*loc. cit.*); (2) *idem*, *Monatsh.*, 1919, 40, 363; (3) Skrabal and Reith, *ibid.*, 1921, 42, 245; (4) Skrabal and Hermann, *ibid.*, 1922, 43, 633.

less error than are the separate  $r$ 's, and probably to a small error only. It is seen from the table that this ratio is 1.45. Now the same ratio can readily be calculated from the molecular model on the basis of certain assumptions. The assumptions which seem best to conform to existing knowledge of the structures and reactions involved are as follows : (1) The distance between the centres of singly linked carbon atoms is 1.52 Å.U., that is, the value obtaining both for the diamond and for the distance between nuclear and side-chain carbon atoms in hexamethylbenzene. (2) The distance between the centres of doubly linked carbon atoms is 1.35 Å.U., this value being adopted on the ground that the aromatic ortho-distance given by X-ray measurements on graphite and hexamethylbenzene probably approximates to the mean of the distances characteristic of singly and doubly linked atoms. (3) Since the carboxyl group is a symmetrical prototropic system, the charge is symmetrically distributed in the carboxylate ion, and its centre of gravity is therefore at the bisection of the line joining the centres of the oxygen atoms, that is, about 0.7 Å.U. from the carbon centre in line with the carbon-carbon bond. (4) In *alkaline* hydrolysis the attack is at the surface of the carbon atom, the mean focus being about 0.7 Å.U. from the carbon centre in line with the carbon-carbon bond. (5) The angle between the directions of the single linkings of an ethenoid carbon atom is 120° (compare Beesley, Ingold, and Thorpe, J., 1915, 107, 1080). On the basis of these assumptions, the ratio  $r_{\text{fumaric}}/r_{\text{maleic}}$  should be 1.47, and almost any reasonable modification of them leads to values between 1.4 and 1.5.

CLXXIX.—*Conversion of Hydroaromatic into Aromatic Compounds. Part IV. The Influence of the Nitro-group in Nitrophenyldihydroresorcinols.*

By LEONARD ERIC HINKEL and JOHN FREDERICK JAMES DIPPY.

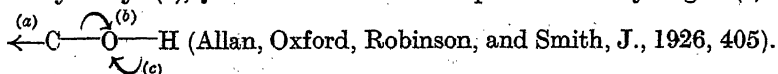
5-m-Nitro- and 5-p-nitro-phenyldihydroresorcinols exhibit properties in common with all dihydroresorcinols, but show a marked difference in their action with the chlorides of phosphorus.

Neither of the nitrophenyldihydroresorcinols reacts with phosphorus trichloride in the usual manner, whereas alkyl- and aryl-substituted dihydroresorcinols yield the corresponding chloro-ketone derivatives with both phosphorus trichloride and phosphorus oxychloride (Crossley and Haas, J., 1903, **83**, 494; Crossley and Le Sueur, *ibid.*, p. 110; Crossley and Pratt, J., 1915, **107**, 191; Boyd, Clifford, and Probert, J., 1920, **117**, 1383).

Phosphorus oxychloride is without action upon *m*-nitrophenyldihydroresorcinol, but yields with the *p*-nitro-compound a small amount of 3 : 5-dichloro-1-*p*-nitrophenyl- $\Delta^{2:4}$ -cyclohexadiene.

Phosphorus pentachloride acts upon *m*-nitrophenyldihydroresorcinol to give 3 : 5-dichloro-1-*m*-nitrophenyl- $\Delta^{2:4}$ -cyclohexadiene together with a small quantity of 3 : 5-dichloro-3'-nitrodiphenyl. In order to effect reaction four molecular proportions of the pentachloride are required instead of the usual two.

The low reactivity of the nitrophenyldihydroresorcinols towards the chlorides of phosphorus may be attributed to the recognised electron-affinity of the nitro-group, since, in any hydroxyl compound, intramolecular electron-attraction (*a*) must oppose the separation of hydroxyl (*b*), just as it assists the separation of hydrogen (*c*) :



The powerful electron-affinity of the nitro-group is also shown by the great readiness with which the nitrobenzaldehydes condense with acetone: our preparative work has convinced us that the order of facility of the condensation of benzaldehydes with acetone is *m*- and *p*-nitro-  $\gg$  methoxy- and chloro-  $>$  unsubstituted benzaldehyde. The position of the nitro-compounds in this sequence is again attributable to the electron-affinity of the nitrophenyl group, since the accepted theory of the aldol reaction involves in its application to the present cases the addition of an anion to aromatic carbonyl carbon.

The effect of the nitrophenyl group upon the properties of the dichlorohexadienes shows no very marked difference from that of

the phenyl group. The chlorination of 3:5-dichloro-1-*m*-nitrophenylcyclohexadiene yields 3:5-dichloro-3'-nitrodiphenyl and 2:3:5(?)-trichloro-3'-nitrodiphenyl (compare Hinkel and Hey, J., 1928, 2786). However, in contrast with the case of the phenyl compound, where trichlorodiphenyl is formed with excess of chlorine in hot solution, the formation of the trichloro-3'-nitrodiphenyl is favoured at low temperature.

The constitution of 3:5-dichloro-3'-nitrodiphenyl has been established by reduction to the amino-derivative and oxidation of this to 3:5-dichlorobenzoic acid.

#### EXPERIMENTAL.

*m*-Nitrobenzylideneacetone.—The method described by Baeyer and Becker (*Ber.*, 1883, **16**, 1969) has been so modified as to need redescription. 0.1*N*-Sodium hydroxide (150 c.c.) was added below 0° to a solution of *m*-nitrobenzaldehyde (30 g.) in acetone (300 c.c.) and the mixture was shaken for 20 minutes, slightly acidified, and evaporated. The orange-coloured liquid residue (probably the aldol intermediate compound) was heated for  $\frac{1}{2}$  hour at 100° with concentrated hydrochloric acid (0.5 c.c.): from a hot alcoholic solution of the dehydrated product, on cooling, *m*-nitrobenzylideneacetone separated in pale yellow needles (25 g.), m. p. 102° (Vorländer, *Annalen*, 1897, **294**, 291, records m. p. 96°) (Found: C, 62.3; H, 4.7. Calc.: C, 62.8; H, 4.7%).

5-*m*-Nitrophenyldihydroresorcinol.—By condensing *m*-nitrobenzylideneacetone with ethyl malonate by Vorländer's method (*loc. cit.*), ethyl *m*-nitrophenyldihydroresorcyate was obtained, m. p. 169° (decomp.); Vorländer records m. p. 163° (Found: C, 59.1; H, 5.15. Calc.: C, 58.8; H, 5.2%).

A solution of the ester (20 g.) in 4% aqueous sodium hydroxide (400 c.c.) was boiled for 5 minutes and cooled, and dilute hydrochloric acid added until the solution became faintly acid; on stirring, a dark brown impurity separated. The filtered solution was boiled with excess of hydrochloric acid until the liberation of carbon-dioxide ceased. The brown solid which separated yielded, on crystallisation from aqueous acetone, 5-*m*-nitrophenyldihydroresorcinol in small plates (14 g.), m. p. 188° (decomp.) (Found: C, 61.8; H, 4.8.  $C_{12}H_{11}O_4N$  requires C, 61.8; H, 4.7%).

5-*p*-Nitrophenyldihydroresorcinol.—The condensation of *p*-nitrobenzylideneacetone with ethyl malonate was conducted in the usual manner and the hydrolysis of the dihydroresorcyate produced was as described above. The solid product when crystallised from aqueous acetone yielded 5-*p*-nitrophenyldihydroresorcinol in faintly brown plates, m. p. 190–191° (decomp.), containing  $1H_2O$  (Found:



C, 57.2; H, 5.2;  $\text{H}_2\text{O}$ , 7.4.  $\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}\cdot\text{H}_2\text{O}$  requires C, 57.2; H, 5.2;  $\text{H}_2\text{O}$ , 7.2%).

*Action of Phosphorus Oxychloride on p-Nitrophenyldihydroresorcinol.*—A suspension of *p*-nitrophenyldihydroresorcinol (5 g.) in dry chloroform (13 c.c.) was mixed with 10 c.c. of phosphorus oxychloride and heated on a water-bath for 2 hours. The chloroform was then removed, and the residue poured into water and extracted with ether. From the extract, washed with sodium hydroxide solution and with water and dried, a small quantity of 3 : 5-dichloro-1-*p*-nitrophenyl- $\Delta^{2:4}$ -cyclohexadiene was obtained, which crystallised from aqueous alcohol in colourless prisms, m. p.  $81^\circ$  (Found : Cl, 26.1.  $\text{C}_{12}\text{H}_9\text{O}_2\text{NCl}_2$  requires Cl, 26.3%).

*Action of Phosphorus Pentachloride on m-Nitrophenyldihydroresorcinol.*—*m*-Nitrophenyldihydroresorcinol (30 g.; 1 mol.) was suspended in dry chloroform (80 c.c.), phosphorus pentachloride (90 g.; 4 mols.) gradually added in the cold, and the mixture heated for  $1\frac{1}{2}$  hours. The chloroform was removed under reduced pressure, and the residue poured on ice and extracted with ether. From the washed and dried extract, 3 : 5-dichloro-1-*m*-nitrophenyl- $\Delta^{2:4}$ -cyclohexadiene was obtained, which crystallised from aqueous alcohol in short colourless needles, m. p.  $66\text{--}68^\circ$  (Found : Cl, 26.3%), together with a small quantity of 3 : 5-dichloro-3'-nitrodiphenyl, m. p.  $162^\circ$  (Found : Cl, 26.35.  $\text{C}_{12}\text{H}_7\text{O}_2\text{NCl}_2$  requires Cl, 26.4%). The separation of the two compounds was effected by fractional crystallisation from methyl alcohol, in which the latter is less soluble.

3 : 5-Dichloro-3'-acetamidodiphenyl.—3 : 5-Dichloro-3'-nitrodiphenyl (0.9 g.), dissolved in alcohol (10 c.c.), was reduced with stannous chloride (3.3 g.) in absolute alcohol (12 c.c.) saturated with hydrogen chloride. The mixture was heated for 1 hour and, after evaporation, excess of sodium hydroxide was added and the base was extracted with ether. It was obtained as a thick oil, from which, by warming with acetic anhydride, 3 : 5-dichloro-3'-acetamidodiphenyl was prepared; this crystallised from aqueous alcohol in colourless plates, m. p.  $168^\circ$  (Found : N, 5.0.  $\text{C}_{14}\text{H}_{11}\text{ONCl}_2$  requires N, 5.0%).

*Oxidation of 3 : 5-Dichloro-3'-aminodiphenyl.*—The oil obtained by the reduction of 3 : 5-dichloro-3'-nitrodiphenyl was dissolved in the minimum quantity of glacial acetic acid and heated under reflux with a solution of chromic anhydride in acetic acid. Further additions of chromic anhydride were made until oxidation was complete. On addition of water, 3 : 5-dichlorobenzoic acid, m. p.  $183\text{--}185^\circ$  after crystallisation from aqueous methyl alcohol, separated.

*Action of Chlorine on 3:5-Dichloro-1-m-nitrophenyl- $\Delta^{2:4}$ -cyclohexadiene.*—(1) *At a low temperature.* Chlorine (1.6 g.; 1 mol.) was passed into a solution of 3:5-dichloro-1-m-nitrophenyl- $\Delta^{2:4}$ -cyclohexadiene (6 g.; 1 mol.) in dry chloroform (16 g.) below 0°. The residue obtained after rapid removal of the chloroform solidified in a vacuum over solid sodium hydroxide and was crystallised from alcohol, 3:5-dichloro-3'-nitrodiphenyl (2.5 g.) being obtained in fine colourless needles which, alone or mixed with the aromatic compound obtained from the phosphorus pentachloride reaction, melted at 162°.

(2) *In excess at a low temperature.* Chlorine was slowly passed into a solution of 3:5-dichloro-1-m-nitrophenyl- $\Delta^{2:4}$ -cyclohexadiene (6 g.) in dry chloroform (25 c.c.) kept at -10°. When chlorine was no longer absorbed, the chloroform was removed and the residue allowed to stand in a vacuum. The sticky mass obtained was dissolved in hot alcohol; on cooling, 2:3:5(?)-trichloro-3'-nitrodiphenyl separated, and after crystallisation from alcohol was obtained as fine colourless needles, m. p. 116° (Found: Cl, 32.0.  $C_{12}H_6O_2NCl_3$  requires Cl, 35.2%). The low chlorine value is probably due to the presence of a small quantity of 3:5-dichloro-3'-nitrodiphenyl.

(3) *In excess at room temperature.* Chlorine was passed into a solution of 3:5-dichloro-1-m-nitrophenyl- $\Delta^{2:4}$ -cyclohexadiene (6 g.) in dry chloroform (16 c.c.) until the copious evolution of hydrogen chloride had ceased. After removal of chloroform and standing in a vacuum, the residue solidified. Crystallisation from alcohol yielded 3:5-dichloro-3'-nitrodiphenyl, m. p. 162°.

The authors wish to express their indebtedness to Imperial Chemical Industries for a grant which partly defrayed the cost of this investigation.

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## CLXXX.—*The Alkaloids of Ergot. Part I.*

By SYDNEY SMITH and GEOFFREY MILLWARD TIMMIS.

It is probably true that no drug of vegetable origin has been more often investigated than ergot and this is not surprising in view of the importance of the drug in medical practice. The earlier researches, which extend backward for more than a century, dealt with undoubtedly impure preparations and the first important advance was made by Tanret (*Compt. rend.*, 1875, **81**, 896), who isolated a pure crystalline alkaloid, ergotinine, which he regarded

as the physiologically active principle. This view of ergotinine was not generally accepted, and for knowledge of the physiologically active alkaloid of ergot we are indebted to the researches of Barger, Carr, and Dale, who at the British Association meeting in 1906 announced the isolation of an amorphous alkaloid, ergotoxine, having the pharmacological effects characteristic of ergot, and to Kraft (*Arch. Pharm.*, 1906, **244**, 336), who independently and almost simultaneously described the same alkaloid under the name hydro-ergotinine. Barger and Carr (*J.*, 1907, **91**, 337) subsequently gave a detailed description of the chemical characteristics of ergotoxine and its salts, and the physiological effects of the alkaloid were fully described by Dale (*Biochem. J.*, 1907, **2**, 240 and elsewhere).

It was shown by Kraft and by Barger and Carr that ergotoxine and ergotinine are interconvertible and by Dale that ergotoxine has an intense physiological activity whereas ergotinine is comparatively inactive. It therefore created considerable interest when Spiro and Stoll (*Verh. Schweiz. Nat. Ges.*, 1920, abstracted in *Ber. ges. Physiol.*, 1921, **8**, 349 and *Chem. Zentr.*, 1921, III, 889—890) described two alkaloids, ergotamine and ergotaminine, which were also interconvertible and one of which, ergotamine, had a much greater biological activity than the other. Moreover, the methods which effected the interconversion of ergotoxine and ergotinine were the same as those which caused the interconversion of ergotamine and ergotaminine. It seemed probable, therefore, that ergotoxine and ergotamine, if not identical, must be closely related, a view which received support when it was shown by Dale and Spiro (*Arch. exp. Path. Pharmacol.*, 1922, **95**, 377) that ergotoxine and ergotamine had the same physiological action not only qualitatively but quantitatively. The identity of pharmacological action was fully confirmed by the subsequent work of Rothlin (*ibid.*, 1928, **138**, 115), Burn and Ellis (*Pharm. J.*, 1927, **64**, 384), and others.

Similarly, some years ago we began an investigation with the object of establishing the chemical identity of ergotoxine and ergotamine or alternatively of more clearly distinguishing the two alkaloids, since the recorded differences were not striking and might possibly be due to variations in the purity of the material used by the respective workers, particularly as ergotoxine had hitherto been obtained only in an amorphous condition.

Ergotoxine can now be obtained in beautifully crystalline form as an additive compound with benzene or its simple homologues (Wellcome Foundation Ltd., and G. M. Timmis, B.P. 286,400), or by crystallisation from carbon disulphide. Crystallisation from such solvents takes place very readily and affords an easy method of purification. The sharp definition of the crystals and the constant

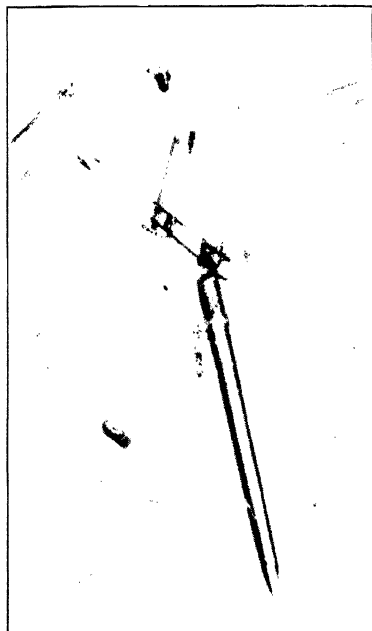
specific rotation leave no doubt concerning the purity of the substance. Ergotoxine cannot according to our experience be crystallised from other solvents and in this respect shows a pronounced difference from ergotamine, which crystallises with great ease from a number of solvents. For the purpose of comparison we have prepared all four alkaloids in a state of purity. The evidence afforded by the crystalline form, specific rotation, solubilities and melting points shows quite clearly that the four alkaloids are definite and distinct substances.

Spiro and Stoll in their publications lay stress on the "protective" methods of extraction devised by Stoll (D.R.-P. 257,272), who suggests (*Naturwiss.*, 1923, **33**, 705) that the failure of other workers to obtain ergotamine may have been due to the use of commercial ergots containing little or no ergotamine either because they were old and deteriorated or because they were originally poor therein, but that the chief cause appeared to have been the use of insufficiently protective methods of extraction.

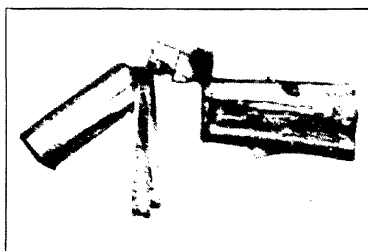
Our experience, on the contrary, has been that the isolation of the alkaloids may be effected satisfactorily by ordinary methods of alkaloid extraction such as that of Kraft (*loc. cit.*). Stoll's process consists essentially in treating the drug with a solution of a weakly acidic substance such as aluminium sulphate, ferrous sulphate, ferric chloride or copper sulphate. The acid material is freed from extractive matter by treatment with a solvent such as benzene or ether. The alkaloid is then set free by treatment with an alkali and extracted with ether or benzene or similar solvent. It is difficult to agree that such a process is less likely to cause decomposition of the alkaloids than the process of Kraft, which consists in extracting the drug with ether, extracting the alkaloids from the ethereal solution with a weak acid such as citric acid, and precipitating the alkaloids from the slightly acid extract by means of a base. In our experience it is immaterial as far as the nature of the alkaloid is concerned whether the alkaloids are prepared by the method of Kraft or by the processes described by Stoll.

During the past few years we have examined many commercial specimens of ergot from Spain, Portugal, Russia, Poland, Scandinavia, Hungary, and Czecho-Slovakia, all of which gave ergotoxine and ergotinine and these alkaloids only. These ergots were all obtained from rye which is the variety used traditionally in medicine and is officially specified by the pharmacopoeias.

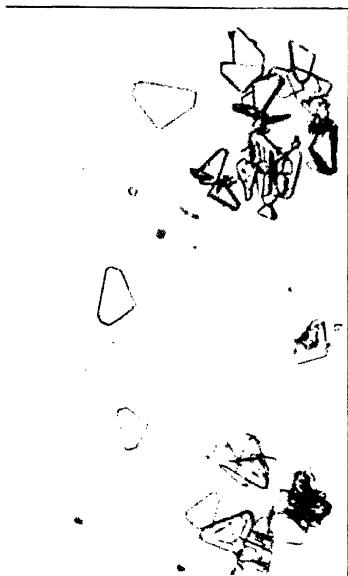
Ergot grows on other *Gramineae* besides rye and we therefore examined some of the unofficial ergots. This part of the investigation is at present incomplete, as these varieties of ergot are difficult to procure. We have, however, been able to obtain three specimens



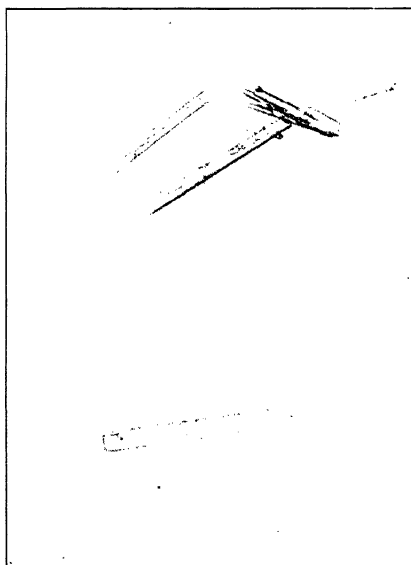
*Ergotinine.*



*Ergotoxine.*



*Ergotaminine.*



*Ergotamine.*



of the ergot growing on tall fescue (*Festuca*), which were collected in New Zealand in 1927, 1928 and 1929. Two of them gave excellent yields of ergotamine, but the third contained comparatively little alkaloid. These ergots were extracted by the method of Kraft.

These results suggest that the isolation of ergotamine and ergotaminine depends not on the special methods of extraction upon which Stoll lays so much stress but upon the nature of the ergot.

In our experience ergot of rye gives ergotoxine and ergotinine only and in this we confirm the results of Tanret, who isolated ergotinine, and of Barger and Carr and of Kraft, who isolated both alkaloids.

Barger and Carr suggested the formulæ  $C_{35}H_{41}O_6N_5$  and  $C_{35}H_{39}O_5N_5$  for ergotoxine and ergotinine, and Spiro and Stoll assigned the formula  $C_{33}H_{35}O_5N_5$  to ergotamine and ergotaminine. Although we have made many analyses of these alkaloids and their salts, we have not succeeded in finding conditions which give completely satisfactory results. Previous workers have experienced this difficulty also and we prefer to reserve a discussion of the composition and inter-relationship of the four alkaloids until these difficulties have been overcome or until we have been able to prepare degradation products which will throw light upon this question.

#### EXPERIMENTAL.

*Isolation of Ergotoxine and Ergotinine.*—The mixed crude alkaloids were prepared from ergot by the method of Kraft (*loc. cit.*), the average yield being 0.1 to 0.15%. The crude alkaloid is treated with methyl alcohol, which dissolves ergotoxine and leaves most of the ergotinine undissolved. The solution of ergotoxine with some ergotinine may then be purified by taking advantage of the different solubilities of the sulphates (Kraft), or purification may be effected by preparing the phosphate (Barger and Carr, *loc. cit.*). The ergotinine residue is readily purified by crystallisation from dilute alcohol.

Ergotoxine was usually prepared from the phosphate by triturating the salt with water and sodium bicarbonate. The mixture was extracted with ether, and the extract evaporated to dryness. The solid residue was dissolved in hot benzene, from which it readily crystallised on cooling in six-sided prisms containing 21% of benzene and having a specific rotation  $[\alpha]_{5461}^{19} = -179^\circ$  and  $[\alpha]_{5790}^{19} = -156^\circ$  ( $c = 1$  in chloroform). Ergotoxine can be crystallised from toluene, the xylenes and mesitylene and separates in each case associated with the solvent, which can be removed by very prolonged drying at  $90^\circ$  in a vacuum. The solvent-free residue has a specific rotation  $[\alpha]_{5461}^{18} = -226^\circ$  and  $[\alpha]_{5790}^{20} = -197^\circ$  ( $c = 1$  in chloroform). Ergot-

oxine is sparingly soluble in carbon disulphide and separates in stout prisms on the spontaneous evaporation of a solution in this solvent. It is insoluble in light petroleum, sparingly soluble in ether, and very soluble in methyl and ethyl alcohol, chloroform and acetone and ethyl acetate, but does not crystallise from these solvents. When an acetone solution is diluted with water, the base separates in an amorphous condition (distinction from ergotamine, which crystallises readily under these conditions). The amorphous base is hygroscopic. The dry substance when placed in a bath at 170° and slowly heated begins to soften at 180° (corr.) and melts very indefinitely between 190° and 200°. It is readily soluble in 1–3% aqueous sodium hydroxide solution but insoluble in sodium carbonate solution.

Ergotinine was most readily purified by crystallisation from hot alcohol containing from 10–50% of water. It crystallised in long, thin, glistening, colourless prisms, free from solvent. It has  $[\alpha]_{5461}^{19} = +513^\circ$ ,  $[\alpha]_{5790}^{19} = +435^\circ$  ( $c = 1$  in chloroform). It is insoluble in light petroleum, very sparingly soluble in pure ether, sparingly soluble in acetone and in methyl and ethyl alcohols, easily soluble in benzene and chloroform. The dry substance when placed in a bath at 200° and slowly heated melts and decomposes at 239° (corr.) after preliminary darkening. Barger and Carr (*loc. cit.*) record decomposition points up to 229° (corr.), but, as pointed out by these authors, the decomposition point is not very characteristic. Ergotinine is insoluble in solutions of alkaline hydroxides or carbonates.

*Isolation of Ergotamine and Ergotaminine.*—The mixed crude alkaloids were prepared from *Festuca ergot* in the same manner as ergotoxine and ergotinine from ergot of rye. The crude alkaloid was treated with three parts of methyl alcohol, which dissolved ergotamine and left a residue of ergotaminine. The methyl-alcoholic extract was diluted with five volumes of ether, and the solution extracted with aqueous citric acid. The acid extracts on basification with sodium carbonate gave a precipitate of ergotamine.

Ergotamine may be purified by preparing the phosphate. The base is dissolved in 10 parts of dry acetone and treated with a solution of phosphoric acid in acetone. The phosphate separates in a semi-crystalline condition and may be recrystallised or converted into the base by treatment with ether and sodium bicarbonate. Ergotamine crystallises readily from aqueous acetone in long rectangular plates containing solvent or less readily from benzene in small needles. It is insoluble in light petroleum, less soluble than ergotoxine in benzene, chloroform and ether, and easily soluble in nitrobenzene and pyridine. The dry substance has specific rotation



$[\alpha]_{5461}^{20} = -181^\circ$  and  $[\alpha]_{5790}^{20} = -159^\circ$  ( $c = 1$  in chloroform). When placed in a bath at  $205^\circ$  and slowly heated, the dry substance melts fairly sharply and decomposes at  $213\text{--}214^\circ$  (corr.) after softening and darkening. It is soluble in a dilute solution of sodium hydroxide but insoluble in aqueous sodium carbonate. Ergotamine isolated from commercial ergotamine tartrate crystallised in the same form as the alkaloid isolated from *Festuca ergot* and after recrystallisation had an identical specific rotation and m. p.

Ergotaminine was prepared by the crystallisation of the crude residue obtained as above. It crystallises from alcohol, acetone, nitrobenzene and ether, pyridine and water, chloroform, and light petroleum. It separates from alcohol in the characteristic thin triangular plates free from solvent as described by Spiro and Stoll or in five-sided plates as illustrated. It is practically insoluble in light petroleum, sparingly soluble in benzene, toluene, methyl and ethyl alcohols, acetone and ethyl acetate, fairly readily soluble in chloroform and nitrobenzene, and easily soluble in pyridine. It has specific rotation  $[\alpha]_{5461}^{18} = +450^\circ$  and  $[\alpha]_{5790}^{18} = +385^\circ$  ( $c = 0.5$  in chloroform). When placed in a bath at  $240^\circ$  and slowly heated, it melts and decomposes at  $252^\circ$  (corr.). It is insoluble in dilute solutions of alkaline hydroxides or carbonates.

Our thanks are due to Mr. A. C. McDougall, B.Sc., and Mr. E. L. Kendrick for the preparation of the photomicrographs which illustrate this paper.

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DARTFORD.

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# CLXXXI.—*The Development of a Novel Form of Isomerism in the Sugar Series. Part II. The Third Variety of Tetra-acetyl Methylmannoside.*

By HAROLD GRAHAM BOTT, WALTER NORMAN HAWORTH, and EDMUND LANGLEY HIRST.

THE discussion opened in Part I of this series dealing with the third variety of triacetyl methylrhamnoside (Haworth, Hirst, and Miller, J., 1929, 2469) has now been extended to the anomalous or third variety of tetra-acetyl methylmannoside. The facts are that three forms of tetra-acetyl methylmannoside exist as crystalline substances, and have the following properties (Dale, J. Amer. Chem. Soc., 1924, 46, 1046):

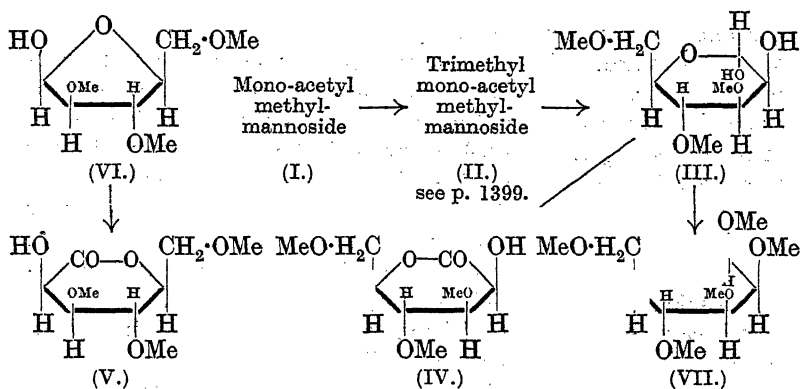
	$\alpha$ -Form.	$\beta$ -Form.	" $\gamma$ "-Form.
M. p. ....	$65^\circ$	$161^\circ$	$105^\circ$
$[\alpha]_D$ in chloroform .....	$+49.1^\circ$	$-46.8^\circ$	$-26.6^\circ$

In discussing the three corresponding triacetyl methylrhannosides we were able to recognise all of them as six-atom ring forms of pyranosides. It will now be shown that the  $\alpha$ -,  $\beta$ -, and " $\gamma$ "-forms of tetra-acetyl methylmannoside are also six-atom ring forms, and there arises the question of how the existence of these three modifications can be reconciled with existing views on stereoisomerism in the sugar group. The proof of the constitution of tetra-acetyl  $\alpha$ -methylmannoside was developed in an earlier communication (Goodyear and Haworth, J., 1927, 3136), and a similar proof of the pyranose structure of tetra-acetyl  $\beta$ -methylmannoside has been completed and will be published soon.

The third or " $\gamma$ "-variety of tetra-acetyl methylmannoside possesses several unique features, the most important of which is that three of the acetyl groups are eliminated by contact with cold alkali but the fourth acetyl group is resistant to hydrolysis even with hot alkali. We have submitted the monoacetyl methylmannoside (prepared by an alternative procedure to that given by Levene and Sobotka, J. Biol. Chem., 1926, 67, 771) to a close investigation, and have found that it behaves in a similar manner to the monoacetyl methylrhannoside which has already been discussed in Part I of this series. On re-acetylation it passes again to the " $\gamma$ "-tetra-acetyl methylmannoside, so there can have been no profound change of structure during the partial de-acetylation process. The monoacetyl methylmannoside (I) gave on methylation *monoacetyl trimethyl methylmannoside* (II). The acetyl group in this substance also exhibits the same resistance towards alkaline reagents that was observed in the original tetra-acetate. It is evident that the monoacetyl trimethyl derivative retains the essential structure of the " $\gamma$ "-tetra-acetyl methylmannoside, a conclusion which is further supported by the ease of hydrolysis of the mannosidic methyl group in either compound with *N*/100-acid in the cold. The trimethyl derivative (II) loses both the mannosidic methyl group and the acetyl group with 2% acid at 100° and yields a crystalline trimethyl mannose which we have designated 3:4:6-*trimethyl mannopyranose* (III), a sugar which gives rise on oxidation to *d*-3:4:6-trimethyl  $\delta$ -mannonolactone (IV), m. p. 96–97°,  $[\alpha]_D + 167.5^\circ$  (in water)  $\rightarrow 110^\circ$ . The corresponding *l*-form (V) of this lactone has already been synthetically prepared by Haworth and Peat from *l*-trimethyl arabofuranose (VI) (J., 1929, 350), and has the same melting point, and the same magnitude of rotation but opposite in sign. From the *d*-lactone the phenylhydrazide of *d*-3:4:6-trimethyl mannonic acid was prepared, and this again has the same m. p. as that of the phenylhydrazide of the *l*-acid obtained by Haworth and Peat. Since the constitution of the

1-3 : 4 : 6-trimethyl  $\delta$ -mannonolactone has been proved both by the method of synthesis and by its conversion into the tetramethyl  $\delta$ -mannonolactone, it will be clear that the *d*-isomeride which has now been isolated must be a six-atom ring form and recognisable under the nomenclature assigned to it in this discussion.

A confirmation of the pyranose structure of the 3 : 4 : 6-trimethyl mannose was developed in the following way. By further methylation the sugar was converted into the crystalline 2 : 3 : 4 : 6-tetramethyl  $\beta$ -methylmannoside (VII) which, in a subsequent publication, will be shown to be capable of hydrolysis to 2 : 3 : 4 : 6-tetramethyl mannopyranose, yielding the characteristic crystalline anilide.



It may be added that the 3 : 4 : 6-trimethyl mannose was crystallised as an  $\alpha$ -form mutarotating from  $[\alpha]_D = +21^\circ \rightarrow 8.2^\circ$ . The rate of hydrolysis of the derived *d*-3 : 4 : 6-trimethyl  $\delta$ -mannonolactone (IV) was studied and was in full agreement with the values observed by Haworth and Peat (*loc. cit.*) for the *l*-isomeride, but with the sign of rotation reversed. Not only so, but the rate of hydrolysis is comparable with that of *d*-tetramethyl  $\delta$ -mannonolactone (Drew, Goodyear, and Haworth, J., 1927, 1237).

From these experiments it is inferred that the monoacetyl methyl-mannoside (I) has the constitution of a six-atom ring form, and that the acetyl group is situated at position 2 of the mannose ring. It is therefore to be formulated as a 2-acetyl derivative of methyl mannopyranoside, and not as a four-atom ring structure as represented by C. S. Hudson (*J. Amer. Chem. Soc.*, 1926, 48, 1434). The unique behaviour associated with this substance is, however, not explained by this simple formulation, since the tetra-acetyl mannoside from which it was derived differs widely in behaviour from the  $\beta$ -tetra-acetyl methylmannoside, in that from the latter the acetyl group at

position 2 is readily eliminated by hydrolysis along with the other three acetyl groups. There is, therefore, some special character associated with the acetyl group at position 2 in the third variety ("γ") of tetra-acetyl methylmannoside, and it is this remarkable feature which must now receive explanation.

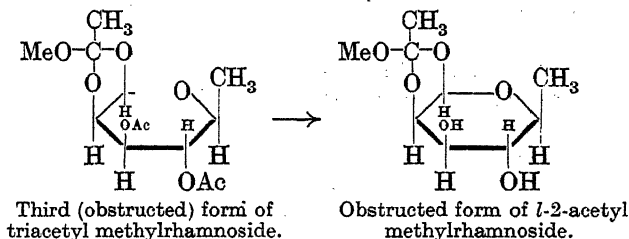
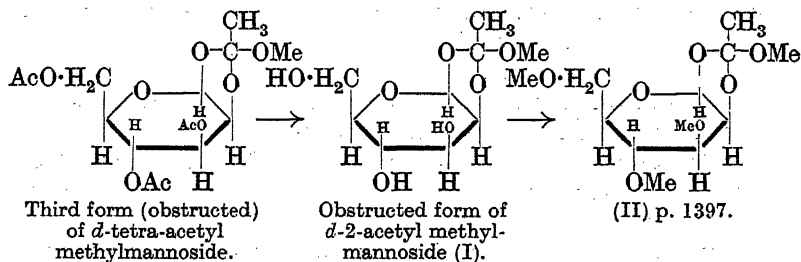
When the above "γ"- or third variety of tetra-acetyl methylmannoside was submitted to methylation with silver oxide and methyl iodide, containing also sodium hydroxide, the product obtained was mainly monoacetyl trimethyl methylmannoside (II) which, on hydrolysis with dilute acid, gave a high yield of crystalline *d*-3 : 4 : 6-trimethyl mannopyranose (IV). On the other hand, the use of excessive quantities of methyl sulphate and alkali effected the replacement of all the acetyl residues by methyl groups, and yielded a mixture of α- and β-forms of tetramethyl methylmannopyranoside from which tetramethyl mannopyranose was afterwards isolated by hydrolysis, and characterised as the crystalline anilide of the latter sugar. The behaviour of the "γ"- or third variety of tetra-acetyl methylmannoside during methylation with these reagents was characteristic. The solution became very dark during the final heating at 100°, and the yield of product was only 40%. Under similar conditions the α- and β-forms of tetra-acetyl methylmannoside give yields which are practically theoretical.

It became evident that, although the replacement of all the four acetyl groups occurred when the "γ"-variety was submitted to this treatment, yet the darkening in colour of the solution was evidence of the intermediate formation of a free sugar, represented by the removal of the mannosidic methyl group simultaneously with the hydrolysis of the acetyl residues. This methyl residue appears to be labile also in contact with dimethylamine and methyl alcohol at 100°.

Still another characteristic feature which clearly differentiates the third or "γ"-variety of the tetra-acetyl or monoacetyl methylmannoside is the ease with which the mannosidic methyl group is hydrolysable with acids of extreme dilution. This property was also remarked upon in the earlier paper dealing with the corresponding rhamnoside. The conclusion there reached was that the resistant acetyl group, which is situated at carbon atom 2 of the pyranose ring, is obstructed by the β-methyl group of the mannoside, and by the proximity of the acetyl group at position 3. It was stated, in the case of the rhamnoside, that this phenomenon might be explicable on the view of the co-ordination of one of the acetoxyl residues with the neighbouring group, and that it was clearly evident that there was restricted movement of the groups attached to carbon atoms, 1, 2, and 3. We suggested as a tentative hypo-

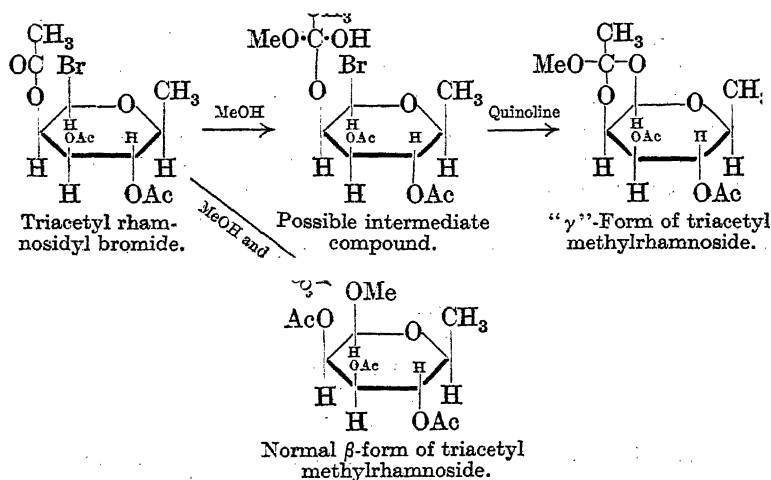
thesis the existence of a strainless ring, which admitted of the interlocking of the groups at carbon atoms 1, 2, and 3.

Simultaneously with the work on this problem we have also been conducting an investigation on the transposition or wandering of acetyl residues in the glucose series, and the following paper illustrates the views which we have been led to adopt as an explanation of this phenomenon. The hypothesis introduced by Fischer that the wandering of acyl residues is accompanied by the intermediate formation of an ortho-carbonic ester type of grouping appears to receive confirmation in the case we have studied, and a similar conception of the existence of an ortho-carbonic ester linking seems to us to apply also to the examples of the third or " $\gamma$ "-varieties of triacetyl methylrhamnoside and tetra-acetyl methylmannoside. The adoption of this view involves both a structural and a stereochemical explanation. The existence of these anomalous compounds, and also the special properties associated with the resistant acetyl group at position 2 in both the rhamnoside and the mannoside, appear to receive a complete explanation from the conclusion that the interlocking of groups at this point in the structure is occasioned by the superposition on the pyranoside structure of a five-atom ring associated through the linking of the groups at carbon atoms 1 and 2.



It must be clearly recognised that the formation of these obstructed forms of methyl-rhamnoside and -mannoside occurs, so far as is at present known, only when the triacetyl rhamnosidyl bromide or tetra-acetyl mannosidyl bromide is submitted to the action of an alcohol in the presence of a base. They do not appear to be formed

by more direct methods. The following scheme may therefore be suggested to explain the mode of formation of these compounds.



(Since it is known that  $\alpha$ -glucosidyl bromides yield  $\beta$ -methylglucosides, a process involving a Walden inversion, the bromine atom is here formulated for the sake of clearness as a  $\beta$ -configuration.)

The alternative view that the resistant acetyl residue is located at position 5 of the rhamnose or mannose chain, and that the sugar ring attaches at positions 1 and 2, has not escaped our consideration. But this alternative is rendered very improbable if only for the fact that a mere change of reagent from quinoline to silver carbonate, in the transformation from the bromide to the rhamnoside, produces a substantial yield of the ordinary unobstructed form of triacetyl  $\beta$ -methylrhamnoside to which has been allocated the pyranose structure.

This formulation for the third varieties of the rhamnoside and mannoside as ortho-carbonic ester derivatives would seem also to provide a reason for the ease with which they undergo hydrolysis with dilute acid when compared with the much greater resistance of the  $\alpha$ - and  $\beta$ -forms to these reagents.

During the preparation of the present paper for the press a communication was received from Professor Freudenberg informing us that he had reached, independently, the same conclusion as ourselves as to the structure herein assigned to the " $\gamma$ "-triacetyl methylrhamnoside, and that a preliminary note by Freudenberg and Braun on this subject was to appear in *Naturwissenschaften*, May 1, 1930.

## EXPERIMENTAL.

*Preparation of "γ"-Monoacetyl Methylmannoside.*—Penta-acetyl mannose was obtained as a liquid containing both the α- and the β-form by treating mannose with acetic anhydride and pyridine at 0° for 4 days. The product was isolated by the method used by Haworth, Hirst, and Miller (*loc. cit.*) for rhamnose tetra-acetate. Tetra-acetyl mannosidyl bromide was then prepared from the liquid penta-acetyl mannose and was converted into "γ"-tetra-acetyl methylmannoside by Dale's method (*loc. cit.*). The latter substance was repeatedly crystallised from ether until it had m. p. 104°, and  $[\alpha]_D^{20} = 27^\circ$  in chloroform, in agreement with the constants recorded by Dale.

The following method was found to be more convenient than the one given by Levene and Sobotka (*loc. cit.*) for the transformation of "γ"-tetra-acetyl methylmannoside into monoacetyl methylmannoside. A solution of the former substance in an excess of *N*/2-alcoholic sodium hydroxide was kept at 0° for 16 hours. After neutralisation by carbon dioxide the solution was filtered and then evaporated to dryness under diminished pressure at 40°. The residue was extracted several times with cold ethyl acetate. Removal of the solvent under diminished pressure at 40° left a viscid syrup, which was obtained as a hygroscopic powder after prolonged drying in a vacuum (yield, 72% of the theoretical).  $[\alpha]_D^{20} = 6^\circ$  (c, 0.83 in water) (Found: C, 46.0; H, 7.1; OMe, 11.2. Calc. for  $C_9H_{16}O_7$ : C, 45.8; H, 6.8; OMe, 13.2%).

Monoacetyl γ-methylmannoside was non-reducing and the acetyl group resisted hydrolysis by 15% aqueous sodium hydroxide at 80°. The substance was, however, readily hydrolysed by dilute acids with loss of methyl and acetyl groups.

*Acetylation of Monoacetyl Methylmannoside.*—A solution of mono-acetyl methylmannoside (2 g.) in pyridine (15 c.c.) and acetic anhydride (21 c.c.) was kept at -5° for 50 hours, and then poured into water. The product was extracted by chloroform, the chloroform solution was neutralised by shaking with aqueous sodium bicarbonate and dried, and the solvent was then removed by distillation under diminished pressure at 35°. After removal of the pyridine by distillation in steam at 35°/11 mm., "γ"-tetra-acetyl methylmannoside was obtained as a colourless crystalline mass (3 g.), m. p. 100°. After recrystallisation from ether the m. p. was 102°. A mixed m. p. determination with an authentic specimen showed no depression.  $[\alpha]_D^{20} = 26.9^\circ$  (c, 1.11 in chloroform) (Found: C, 49.5; H, 6.2; OMe, 8.3. Calc. for  $C_{15}H_{22}O_{10}$ : C, 49.7; H, 6.1; OMe, 8.6%).

*Methylation of Monoacetyl Methylmannoside.*—(a) *By means of*

*silver oxide and methyl iodide.* A solution of monoacetyl methylmannoside (7 g.) in methyl alcohol (7 c.c.) and methyl iodide (70 c.c.) was heated at 30° with silver oxide (20 g.) until the reaction had commenced, and this proceeded for some time without further heating. Silver oxide was added from time to time (70 g. in all) and the temperature was gradually raised to 45°. At the end of 6 hours the product was extracted by chloroform and after isolation was remethylated in the usual way with silver oxide (30 g.) and methyl iodide (30 c.c.). It was then distilled, giving *monoacetyl trimethyl methylmannoside* (6.3 g.) as a colourless liquid, b. p. about 120°/0.1 mm.;  $n_D^{25}$  1.4594;  $[\alpha]_D^{25}$  -20° (c, 1.24 in water);  $[\alpha]_D^{25}$  -11° (c, 1.0 in chloroform) (Found: C, 51.8; H, 8.1; OMe, 42.0.  $C_{12}H_{22}O_7$  requires C, 51.8; H, 7.9; OMe, 44.7%).

(b) *By means of methyl sulphate.* Monoacetyl methylmannoside (5 g.), dissolved in acetone (30 c.c.) and water (10 c.c.), was treated at 50° with methyl sulphate (50 c.c.) and 30% aqueous sodium hydroxide (150 c.c.), the solution being maintained strongly alkaline throughout. (During the methylation there is a tendency for the formation of coloured decomposition products, and it is desirable to omit the usual heating for one hour at 90–100° at the end of the reaction.) The product (2.5 g.), which was isolated in the usual way, had b. p. about 120°/0.1 mm.,  $n_D^{25}$  1.4582,  $[\alpha]_D^{25}$  -23° (c, 1.0 in water). The identity of this material with the monoacetyl trimethyl methylmannoside described above was established by the conversion of both into the same crystalline trimethyl mannose, the yield in each case being over 90% of the theoretical.

The acetyl group in monoacetyl trimethyl "γ"-methylmannoside resisted hydrolysis by aqueous sodium hydroxide, no measurable amount of acetic acid being liberated during 50 hours when a solution of the substance in 3% aqueous alkali was kept at 15°. During this period the specific rotation remained unaltered. In hot aqueous alkali monoacetyl trimethyl "γ"-methylmannoside was slightly unstable, as was shown by the formation of coloured decomposition products. Fehling's solution was reduced to a small extent after prolonged boiling. The amount of decomposition was, however, minute even after treatment with 3% aqueous sodium hydroxide at 50° for 2 hours, since under these conditions 0.191 g. of substance accounted for only 0.2 c.c. of alkali. Further evidence of decomposition in the presence of alkali was provided by the marked development of colour during the simultaneous deacetylation and methylation of monoacetyl trimethyl "γ"-methylmannoside by means of methyl sulphate and strong alkali (see below).

Monoacetyl trimethyl methylmannoside was extremely sensitive to dilute hydrochloric acid. The specific rotation in *N*/100-acid at



20° changed in 60 minutes from  $[\alpha]_D^{20} - 25^\circ$  to the constant value  $+ 2^\circ$ . The liquid then vigorously reduced warm Fehling's solution.  $[\alpha]_D^{20} - 20^\circ$  (4 mins.);  $- 13^\circ$  (10 mins.);  $- 6.4^\circ$  (20 mins.);  $- 1.6^\circ$  (30 mins.);  $+ 0.4^\circ$  (45 mins.);  $2^\circ$  (60 mins.; constant value). No acetic acid was liberated during this period, since a solution of 0.1889 g. of substance in 26.8 c.c. of *N*/100-hydrochloric acid required for neutralisation after 60 minutes 27.0 c.c. of *N*/100-sodium hydroxide. Complete hydrolysis of the acetyl group would involve the liberation of acetic acid equivalent in this case to an additional 68.2 c.c. of *N*/100-alkali. The removal of the acetyl group was effected by the use of *N*/2-sulphuric acid at 90° for 60 minutes (Found:  $\text{CH}_3\text{CO}$ , 14.0. Calc., 15.5%).

3 : 4 : 6-Trimethyl Mannopyranose.—The following series of experiments was carried out in duplicate with material obtained respectively by methods (a) and (b) of the preceding section. The products were identical, and it is only necessary, therefore, to describe one set of experiments.

Monoacetyl trimethyl methylmannoside was dissolved in *N*/2-hydrochloric acid and heated on the water-bath for 90 minutes. The solution was neutralised with barium carbonate, filtered, and evaporated to dryness under diminished pressure. The product was extracted with chloroform and distilled, giving 3 : 4 : 6-trimethyl mannopyranose as a syrup, b. p. about 135°/0.04 mm.,  $n_D^{18}$  1.4734. This soon crystallised and, on recrystallisation from ether, d-3 : 4 : 6-trimethyl  $\alpha$ -mannopyranose was obtained, m. p. 101–102°,  $[\alpha]_D^{20} + 36^\circ$  (c, 0.8 in methyl alcohol),  $[\alpha]_D^{20} + 21^\circ$  (c, 1.04 in water; initial value). Yield, 90% of the theoretical (Found: C, 48.7; H, 8.3; OMe, 40.9.  $\text{C}_9\text{H}_{18}\text{O}_6$  requires C, 48.7; H, 8.1; OMe, 41.8%).

The mutarotation of 3 : 4 : 6-trimethyl mannopyranose in aqueous solution at 22° was complete in about 90 minutes, the equilibrium value being  $[\alpha]_D^{20} + 8.2^\circ$ :  $[\alpha]_D^{20} + 19^\circ$  (3 mins.);  $18.5^\circ$  (5 mins.);  $11.5^\circ$  (30 mins.);  $10^\circ$  (45 mins.);  $8.2^\circ$  (90 mins., constant value). From these figures the initial value was obtained by extrapolation.

3 : 4 : 6-Trimethyl mannopyranose (1.0 g.) was methylated by means of methyl iodide (30 c.c.) and silver oxide (10 g.), the addition of methyl alcohol (2 c.c.) being necessary to effect solution. The mixture was heated at 35° for 3 hours and then allowed to boil gently for an additional 4 hours. The product, after being remethylated in the usual way, crystallised (yield, 0.95 g.). On distillation crystalline tetramethyl  $\beta$ -methylmannopyranoside was obtained mixed with 12% of the  $\alpha$ -isomeride, b. p. about 90°/0.04 mm.,  $n_D^{18}$  1.4521 (supercooled liquid),  $[\alpha]_D^{20} - 65^\circ$  (c, 0.7 in water). Recrystallisation from light petroleum (b. p. 40–60°) gave pure tetramethyl  $\beta$ -methylmannopyranoside as long needles, m. p.

36—37°, alone or when mixed with an authentic specimen,  $[\alpha]_D^{25} - 78^\circ$  (c, 0.4 in water).

*d*-3 : 4 : 6-Trimethyl  $\delta$ -Mannonolactone.—3 : 4 : 6-Trimethyl manno-pyranose (3.7 g.) was dissolved in water (25 c.c.) and treated at 35—40° with bromine (4.5 c.c.) for 2 days; the solution was then found to be non-reducing. After removal of the remaining bromine by aeration the solution was neutralised with silver oxide, the organic acid liberated from its silver salt by titration with hydrochloric acid, the water removed by distillation under diminished pressure, and the product dissolved in ether in order to remove a small quantity of inorganic matter. Evaporation of the ether left crystalline *d*-3 : 4 : 6-trimethyl  $\delta$ -mannonolactone (3.2 g.) which, after recrystallisation from ether, had m. p. 96—97°,  $[\alpha]_D^{25} + 167.5^\circ$  (c, 0.7 in water). These constants are in excellent agreement with those recorded by Haworth and Peat for the corresponding *l*-3 : 4 : 6-trimethyl  $\delta$ -mannonolactone (*loc. cit.*), which has m. p. 96—97° and  $[\alpha]_D - 167^\circ$ .

The phenylhydrazide of *d*-3 : 4 : 6-trimethyl mannonic acid was prepared by heating the lactone (0.2 g.) with the calculated quantity of phenylhydrazine in benzene solution for 30 minutes on the water-bath. The product (0.3 g.) crystallised completely and had m. p. 137—139°, unaltered by recrystallisation from benzene. The m. p. of the *l*-isomeride is 137—139°.

The hydrolysis of the lactone in aqueous solution was followed polarimetrically:  $[\alpha]_D^{20} + 167.5^\circ$  (5 mins.); 167° (30 mins.); 162° (1.5 hrs.); 154° (4.5 hrs.); 147° (8 hrs.); 125° (24.5 hrs.); 118° (32 hrs.); 110° (74 hrs., constant value). If the sign of rotation be reversed, these figures are in excellent agreement with those recorded by Haworth and Peat for the *l*-isomeride.

The rotation of the acid in aqueous solution was measured in the manner described in previous papers:  $[\alpha]_D^{20} + 31^\circ$  (c, 0.7, calc. as lactone; initial value); 39° (1 hr.); 62° (4.5 hrs.); 103° (23 hrs.); 107° (30 hrs.); 111° (48 hrs., constant value). The proportion of lactone present at equilibrium was therefore 58%.

*Attempted Simultaneous Deacetylation and Methylation of "γ"-Tetra-acetyl Methylmannoside by Means of Methyl Iodide and Silver Oxide in the Presence of Solid Sodium Hydroxide.*—Silver oxide (70 g.) and solid sodium hydroxide (6 g.) were added to a solution of "γ"-tetra-acetyl methylmannoside (10 g.) in methyl iodide (50 c.c.). The mixture was heated at 45° for 8 hours. The product (9 g.) was extracted by chloroform and subjected to a second treatment under similar conditions, and was then distilled, giving a colourless viscid syrup (6 g.), b. p. about 120°/0.1 mm.,  $n_D^{25}$  1.4601,  $[\alpha]_D^{25} - 16^\circ$  in chloroform (Found: C, 51.8; H, 8.5; OMe, 45.1%). The material

was therefore mainly monoacetyl trimethyl methylmannoside, and the correctness of this view was proved by hydrolysis with *N*/5-hydrochloric acid at 95°. During 2 hours the specific rotation altered from  $[\alpha]_D^{20} - 7^\circ$  to  $+ 4^\circ$ . The product, which was isolated in the usual way, was 3:4:6-trimethyl mannopyranose, m. p. 101° (yield, 90%).

Similar experiments with silver oxide and solid sodium hydroxide were carried out on monoacetyl trimethyl methylmannoside, but in no case could the acetyl group be removed, and the monoacetyl trimethyl methylmannoside was recovered unchanged.

*Simultaneous Deacetylation and Methylation by Means of Methyl Sulphate and Alkali.*—“ $\gamma$ ”-Tetra-acetyl methylmannoside (5.5 g.), dissolved in acetone (15 c.c.), was treated at 50° with a large excess of methyl sulphate (55 c.c.) and 30% aqueous sodium hydroxide (140 c.c.). During the final heating at 100° for 1 hour the solution became very dark. The product was methylated three times by Purdie's reagents and distilled, giving a colourless liquid, b. p. about 85°/0.03 mm.,  $n_D^{20}$  1.4530,  $[\alpha]_D^{20} - 15^\circ$  (c, 0.9 in water),  $[\alpha]_D^{20} - 7^\circ$  (c, 0.7 in chloroform). Yield, 40% (Found: OMe, 58.2. Calc. for the tetramethyl methylmannoside, 62%). During hydrolysis with 6% hydrochloric acid at 80° the specific rotation altered from  $[\alpha]_D^{20} - 15^\circ$  to the constant value  $[\alpha]_D^{20} + 14^\circ$ . The product was a syrup which, when boiled with aniline in ethyl-alcoholic solution, gave tetramethyl mannopyranose anilide, m. p. 140–142°, alone or in admixture with an authentic specimen. The overall yield of syrupy tetramethyl mannopyranose from “ $\gamma$ ”-tetra-acetyl methylmannoside was 25% of the theoretical, and the minimum yield of crystalline anilide from the tetramethyl mannopyranose was 70%.

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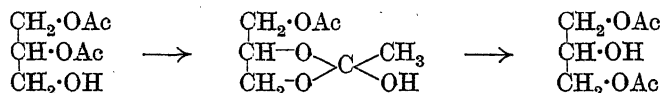
[Received, May 19th, 1930.]

## CLXXXII.—*The Conversion of 1:2:3:4-Tetra-acetyl $\beta$ -D-Glucose into 2:3:4:6-Tetra-acetyl $\beta$ -Methylglucoside.*

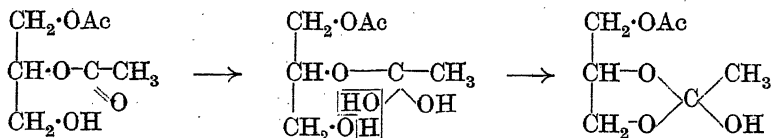
By WALTER NORMAN HAWORTH, EDMUND LANGLEY HIRST, and  
ETHEL GERTRUDE TEECE.

VARIOUS examples are known of the wandering of acyl groups linked with polyhydric alcohol residues. One of the first to observe this change was Fischer (*Ber.*, 1920, 53, 1624), who suggested that the mechanism of the wandering of acyl groups might be explained

by the intermediate formation of an ortho-carbonic ester group of the type shown below :

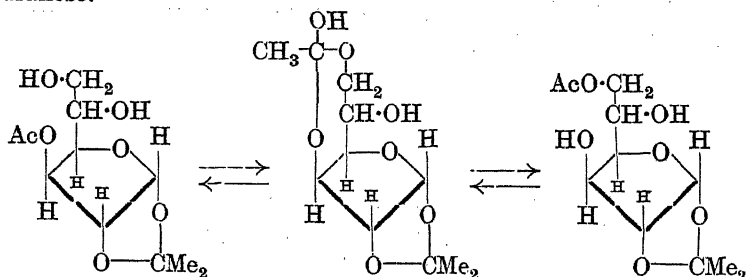


This view may be expanded by including the assumption that the addition and elimination of water takes place in the following way :



Similar instances of acyl wandering are known in the glycerides of higher fatty acids (Grün, *Ber.*, 1921, 54, 290; Fairbourn and Cowdrey, J., 1929, 129; Fairbourn, *ibid.*, pp. 1151, 2232; Hibbert and Carter, *J. Amer. Chem. Soc.*, 1929, 51, 1607) and also in the sugar group (Ohle, *Ber.*, 1924, 57, 403; Ohle and Dickhäuser, *Ber.*, 1925, 58, 2593). A benzoyl or acetyl residue at position 3 in glucose is shown to be capable of translation to position 6, especially under the influence of faintly alkaline solutions, and the conditions under which this change is effected have been studied (Josephson, *Annalen*, 1929, 472, 217).

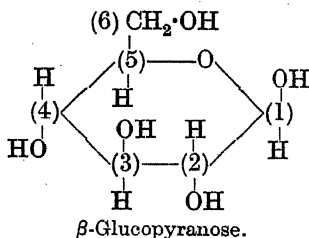
If the above mechanism be admitted, it would appear that the cases studied by the last author may be expressed as follows, where positions 1 and 2 are linked by an acetone group in glucofuranose.



The spatial proximity of the hydroxyls at positions 3 and 6 which are situated at the same side of the plane constituting the glucose ring apparently facilitates this interchange, and these stereochemical considerations are probably of importance also in other cases. In the course of our work on the properties of 1:2:3:4-tetra-acetyl  $\beta$ -glucose (I) (Oldham, J., 1925, 127, 2840; Helferich and Klein, *Annalen*, 1926, 450, 219) we were impressed by the similar

melting points of this substance, of the 2 : 3 : 4 : 6-tetra-acetyl  $\beta$ -glucose (II) (Fischer and Delbrück, *Ber.*, 1909, 42, 2778), and of the supposed 1 : 2 : 3 : 6-tetra-acetyl glucose (III) of Helferich and Klein (*Annalen*, 1927, 455, 173), and by the statement that the pyridine derivative of the supposed 1 : 2 : 3 : 6-tetra-acetyl glucose (III) mutarotates in water from the value  $[\alpha]_D - 22^\circ$  to about that of *D*-glucose ( $+ 53^\circ$ ). Since the simple mutarotation of a compound acetylated in position 1 may be considered unusual, the possibility arose that this last-named compound (III) was structurally closely related to the 2 : 3 : 4 : 6-tetra-acetyl  $\beta$ -glucose (II), which mutarotates from a negative value, in ethyl alcohol, to  $+ 81^\circ$ , and has a melting point almost identical with that of Helferich's supposed 1 : 2 : 3 : 6-tetra-acetyl glucose (III). We have confirmed, by mixed melting-point determinations, the statement that these two substances are not identical, and another explanation must therefore be provided for the properties of (III). It has been shown already that compound (III) passes by methylation into 2 : 3 : 4 : 6-tetra-acetyl  $\beta$ -methylglucoside (Helferich and Klein, *loc. cit.*) and that the acetylated sugar (III) exists in equilibrium with 1 : 2 : 3 : 4-tetra-acetyl  $\beta$ -glucose (I) in very dilute alkali, and is prepared from the latter by this reaction. Helferich has tentatively suggested that the acetyl group which wanders is that at position 4 in the latter compound (I), but has recognised that a further transposition of acetyl residues must occur when (III) undergoes conversion, although in indifferent yield, into tetra-acetyl  $\beta$ -methylglucoside.

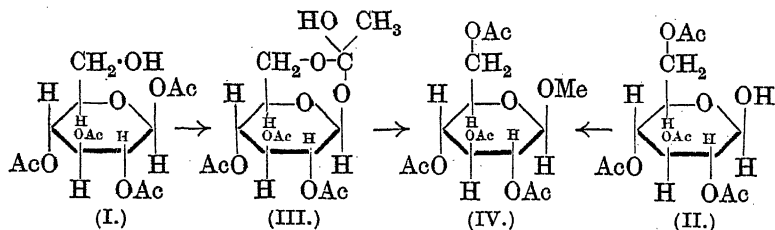
It is seen, however, that position 4 is remote from position 6 in that these hydroxyl groups are situated in different planes in the  $\beta$ -glucopyranose configuration given below.



The possibility that the exchange of acetyl groups may occur from position 3 to 6 has been considered and rejected by Helferich, since the *p*-toluene-sulphonyl derivative of (III) is different from that prepared by Freudenberg and Ivers (*Ber.*, 1922, 55, 929).

Experiments which we have carried out lead definitely to the view that, in the isomerisation of (I) to give (III), the hydroxyls involved are those at positions 1 and 6. We have submitted both 1 : 2 : 3 : 4-tetra-acetyl  $\beta$ -glucose (I) and 2 : 3 : 4 : 6-tetra-acetyl  $\beta$ -glucose (II) to methylation with methyl iodide and silver oxide and have obtained in both cases 2 : 3 : 4 : 6-tetra-acetyl  $\beta$ -methylglucoside (IV) as our product. It is important to note that the migration is not in any way connected with the actual process of

methylation, but is an example of that type of isomerisation which has been referred to above as taking place in certain partially acylated substances under the influence of alkali. Our observations support the result recorded by Helferich, who has obtained the same product (IV) by methylation of the converted tetra-acetyl glucose (III), and we are therefore of opinion that this evidence points to the formulation of (III) as a derivative of ortho-acetic acid originating from (I) in the following way.



Helferich has demonstrated that the pyranose ring remains undisturbed during the change from (I) to (III), since both give rise on acetylation to the usual penta-acetyl glucose.

At present the evidence of the *p*-toluenesulphonyl derivatives of (I) and (III) throws little light on this view of the structure allocated to (III), although it is not inconsistent with it. Before the problem is finally decided, the toluenesulphonyl derivative of (III) will require further study.

#### EXPERIMENTAL.

**1:2:3:4-Tetra-acetyl  $\beta$ -D-Glucose.**—This substance was prepared by the action of hydrogen bromide, dissolved in glacial acetic acid, on 6-trityl 1:2:3:4-tetra-acetyl  $\beta$ -D-glucose (Helferich and Klein, *Annalen*, 1926, 450, 219). Crystallisation from ether gave colourless needles, m. p. 127°,  $[\alpha]_D^{20} + 13^\circ$  (*c*, 2.95 in chloroform). These constants and the properties of the substance are in complete agreement with those given by Helferich and Klein, but the m. p. and rotation are very close also to those of 2:3:4:6-tetra-acetyl  $\beta$ -D-glucose, which, when prepared from tetra-acetyl glucosidyl bromide by the method of Fischer and Delbrück (*Ber.*, 1909, 42, 2778), has m. p. 135°,  $[\alpha]_D^{20} + 16^\circ$  (*c*, 0.87 in chloroform);  $[\alpha]_D^{20} - 1.5^\circ$  (in ethyl alcohol; *c*, 1.17)  $\longrightarrow + 81^\circ$  in 10 days. The two substances are not, however, identical, since the m. p. of a mixture showed a depression of 20–25°. A similar depression was observed when either 1:2:3:4-tetra-acetyl  $\beta$ -D-glucose or 2:3:4:6-tetra-acetyl  $\beta$ -D-glucose (m. p. 135°) was mixed with Helferich's supposed 1:2:3:6-tetra-acetyl  $\beta$ -D-glucose, prepared from the 1:2:3:4-compound by the action of very dilute alkali.

*Methylation of 1:2:3:4-Tetra-acetyl β-d-Glucose.*—A solution of 1:2:3:4-tetra-acetyl β-*d*-glucose (3 g.) in methyl iodide (8 c.c.) was boiled for 8 hours during the gradual addition of dry silver oxide (15 g.) which had been prepared from silver nitrate and barium hydroxide and very thoroughly washed. The product was extracted by boiling chloroform and, on removal of the solvent under diminished pressure, was obtained as a pale yellow viscid syrup (2.8 g.). After being kept for some weeks, this began to crystallise, the rate of crystallisation being increased when the syrup was rubbed with alcohol. The solid was then recrystallised from absolute alcohol, giving colourless needles, m. p. 104–106° (yield, 0.6 g.);  $[\alpha]_D^{22} - 18.5^\circ$  (c, 1.62 in chloroform). The substance did not reduce boiling Fehling's solution. It was identified by a mixed m. p. determination as tetra-acetyl β-methylglucoside, which has m. p. 104–105°;  $[\alpha]_D^{20} - 18.2^\circ$  in chloroform (Found: C, 49.8; H, 6.5; OMe, 9.1. Calc. for C<sub>15</sub>H<sub>22</sub>O<sub>10</sub>: C, 49.7; H, 6.1; OMe, 8.6%).

The syrup left after removal of the tetra-acetyl β-methylglucoside gave OMe, 14.5%, from which it appeared that the methylation process had been accompanied by simultaneous deacetylation.

*Methylation of 2:3:4:6-Tetra-acetyl β-d-Glucose.*—2:3:4:6-Tetra-acetyl β-*d*-glucose (4.2 g.) was dissolved by gentle heating in methyl iodide (15 c.c.). The solution was heated with silver oxide (10 g.) for 6 hours at 45°. The product (4.3 g.), which crystallised spontaneously, m. p. 96°, was mainly 2:3:4:6-tetra-acetyl β-methylglucoside. One crystallisation from alcohol gave pure material, m. p. 105° alone or when mixed with authentic 2:3:4:6-tetra-acetyl β-methylglucoside which had been prepared by the acetylation of β-methylglucoside.

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## CLXXXIII.—*The Hydrolysis of Diacetyl-o-diamines.*

By MONTAGUE ALEXANDRA PHILLIPS.

THE view that *o*-diamines are produced as intermediates in the formation of benziminazoles by the hydrolysis of diacetyl-*o*-diamines (J., 1928, 2393) has now been shown to be only partly correct. The acid hydrolysis of 4-nitro-1:2-diacetamidobenzene and of 5-nitro-1:2:4-triacetamidobenzene proceeds in two directions with the formation of the benziminazole and, to a less extent, of 4-nitro-1:2-diaminobenzene and 5-nitro-1:2:4-triaminobenzene respectively.

If the reaction is stopped when the acetyl compound is largely unchanged, a considerable quantity of the benziminazole, mixed with some diamine (or triamine) can be isolated; at the completion of the hydrolysis, the proportion of ring compound to amine is unchanged, although the amounts are greater. When the reaction is continued, the amount of amine decreases at a rate independent of the concentration of the mineral acid and corresponding with the rate of reaction between the *o*-diamine and acetic acid in the presence of mineral acid; a corresponding increase in the amount of cyclic compound occurs.

Although the rate of hydrolysis in the first stage depends on the concentration of mineral acid, the proportion of *o*-diamine to the ring compound is independent of this. It is possible that the first stage involves hydrolysis to the monoacetyl derivative, especially as it has been shown (Phillips, J., 1928, 172) that *o*-aminoacetanilide is formed together with 2-methylbenziminazole by acid hydrolysis of diacetyl-*o*-phenylenediamine. Although no monoacetyl derivative was isolated in the hydrolysis of 4-nitro-1:2-diacetamidobenzene, owing possibly to its lability, it was found that 4-nitro- and 5-nitro-2-aminoacetanilides behave with boiling hydrochloric acid as does 4-nitro-1:2-diacetamidobenzene, *i.e.*, 4-nitro-1:2-diaminobenzene and 5-nitro-2-methylbenziminazole are both produced and the latter increases in amount at the expense of the former as the reaction proceeds.

When methyl-alcoholic hydrogen chloride is used as the hydrolysing agent, acetic acid is removed as methyl acetate as it is formed, and the cyclic compound obtained must be produced from the diacetyl derivative (possibly, however, with the transient formation of monoacetyl derivatives). It is known that the ring compounds are stable to hot concentrated hydrochloric acid, hence the diamine also is formed from the diacetyl compound. At 80°, with 4-nitro-1:2-diacetamidobenzene, the proportion of 4-nitro-1:2-diaminobenzene to the benziminazole was greater than that found in a similar hydrolysis with aqueous hydrochloric acid, and was unchanged after several hours; at 160°, the yield of the diamine was 96%. Analogous results were obtained with 5-nitro-1:2:4-triacetamidobenzene.

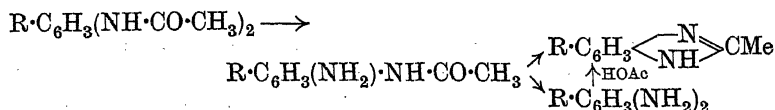
The use of methyl alcohol and the formation of methyl acetate would account for the formation of amino-ketones from diacyl-diaminoethylenes (Windaus, Dorries, and Jensen, *Ber.*, 1921, 54, 2754); in the absence of the alcohol, it is probable that a glyoxaline would be formed.

With diacetyl-*o*-phenylenediamine and hot hydrochloric acid, the reaction proceeds rapidly to give the benziminazole, no diamine



being found even with limited hydrolysis. However, by the use of methyl-alcoholic hydrogen chloride at 160°, *NN'*-dimethyl-*o*-phenylenediamine was obtained, no ring compound being detected.

Taking into consideration all these facts, it is probable that the hydrolysis of diacetyl-*o*-diamines follows the course



The action of caustic alkali on the nitrodiacetyl-*o*-diamines proceeds in the same way, except that the proportion of nitro-diamine to cyclic compound is independent of the time of heating, since 4-nitro-1 : 2-diaminobenzene is unchanged by sodium acetate and sodium hydroxide at 100°. With diacetyl-*o*-phenylenediamine and 25% caustic alkali solution, the ring compound only was detected.

The reduction of 2 : 4-dinitroacetanilide, giving 4-nitro-2-aminoacetanilide, was accompanied by the formation of 5-nitro-2-methylbenziminazole; monoacetylation of 4-nitro-1 : 2-diaminobenzene yielded, in addition to 5-nitro-2-aminoacetanilide, the same cyclic compound. Since the solution was alkaline (ammonia) in the former case and acid (acetic acid only) in the latter, it seems that the ring compound in both cases is formed directly from the initial material.

In the 1-methylbenziminazole series, similar principles probably apply. Treatment of 4-nitro-2-acetamidomethylaniline with methyl-alcoholic hydrogen chloride gave a mixture of 5-nitro-1 : 2-dimethylbenziminazole and 4-nitro-2-aminomethylaniline; as before, both compounds must have been formed independently from the initial material. With hot aqueous hydrochloric acid, no estimation of the rate of disappearance of the methylaniline derivative was recorded; the time after which the *pure* cyclic compound was obtained, however, corresponded with the time after which the *pure* cyclic compound was formed from the methylaniline derivative and acetic acid in the presence of a mineral acid. Shorter periods of heating gave a mixture of the cyclic compound and 4-nitro-2-aminomethylaniline.

The nitration of 5(or 6)-acetamido-2-methylbenziminazole gives 6(or 5)-nitro-5(or 6)-acetamido-2-methylbenziminazole, which was oriented by deamination of the corresponding *amino*-compound, 5(or 6)-nitro-2-methylbenziminazole being formed in good yield. 1 : 2 : 4-Triacetamidobenzene on nitration gives the 5-nitro-derivative, which was oriented by conversion into 6(or 5)-nitro-5(or 6)-amino-2-methylbenziminazole. The orientation of 5-nitro-1 : 2 : 4-triaminobenzene follows from this and also from its reduction to 1 : 2 : 4 : 5-tetra-aminobenzene (compare Nietzki and Hagenbach,

*Ber.*, 1887, 20, 329). Reduction of 5(or 6)-nitro-6(or 5)-acetamido-2-methylbenziminazole gives 5(or 6)-amino-6(or 5)-acetamido-2-methylbenziminazole; this compound and 5(or 6)-diacetamido-2-methylbenziminazole on treatment with boiling dilute mineral acids pass rapidly into  $\alpha$ -2 : 2'-dimethylbenzbisiminazole (compare Nietski and Hagenbach, *loc. cit.*), which is also obtained readily from 1 : 2 : 4 : 5-tetra-aminobenzene or 5 : 6-diamino-2-methylbenziminazole (compare Kym and Ratner, *Ber.*, 1912, 45, 3249) by treatment with acetic and hydrochloric acids. In the presence of formic and hydrochloric acids,  $\alpha$ -2-methylbenzbisiminazole is obtained from 5 : 6-diamino-2-methylbenziminazole, and  $\alpha$ -benzbisiminazole from the tetra-aminobenzene.

5(or 6)-Nitro-2-methylbenziminazole-6(or 5)-arsinic acid, prepared from 5(or 6)-nitro-6(or 5)-amino-2-methylbenziminazole by the Bart reaction, gives the amino-derivative on reduction.

#### EXPERIMENTAL.

4-Nitro-2-aminoacetanilide.—2 : 4-Dinitroacetanilide (10 g.) was boiled for 15 minutes with ammonium sulphide solution (6%, 50 c.c.); on acidification to Congo-red with hydrochloric acid and addition of excess of sodium acetate to the filtered solution, 7 g. of mixed bases were obtained. By digestion with 2*N*-caustic soda solution, 5-nitro-2-methylbenziminazole (3.8 g., m. p. 221°, crystallised from alcohol. Found: N, 23.6. Calc.: N, 23.7%) was extracted; it was precipitated from the alkaline solution with acetic acid. The residue, after crystallisation from alcohol (80%), melted at 205° and was shown to be 4-nitro-2-aminoacetanilide (1.8 g.). It was completely soluble in excess of dilute mineral acids, readily soluble in alcohol or acetic acid, and insoluble in water (Found: N, 21.5.  $C_8H_9O_3N_3$  requires N, 21.5%).

5-Nitro-2-aminoacetanilide.—4-Nitro-1 : 2-diaminobenzene (5.4 g.) was dissolved in 20 c.c. of water with 5 c.c. of hydrochloric acid (*d* 1.16). On addition of acetic anhydride (10 c.c.), followed rapidly by excess of solid sodium acetate (until acidity to Congo-red was removed), the nitro-diamine was reprecipitated as a red solid; this rapidly became yellow as it was acetylated. After 15 minutes, the solid was collected and digested with 2*N*-caustic soda solution; this removed 2.6 g. of 5-nitro-2-methylbenziminazole (m. p. 221° after crystallisation from alcohol. Found: N, 23.7%). The residue (1.6 g.) was crystallised from alcohol until it melted at 195°; it was shown to be 5-nitro-2-aminoacetanilide by the solubility in mineral acids (excess), insolubility in alkalis, and analysis (Found: N, 21.4%). It is sparingly soluble in cold alcohol and insoluble in water or ether, and is a much weaker base than the isomeric 4-nitro-derivative.

5(or 6)-Nitro-6(or 5)-acetamido-2-methylbenziminazole.—5(or 6)-Acetamido-2-methylbenziminazole (9 g.), mixed with potassium nitrate (5 g.), was added at 0–5° to sulphuric acid (60 c.c.); after 1 hour, the mixture was poured into ice-water (1 l.) and basified at 50° with 15% aqueous ammonia. The voluminous yellow mass was collected, washed with water, and crystallised from 50% alcohol (yield, 7.7 g. or 70%). No trace of isomerides was detected in the liquors. 5(or 6)-Nitro-6(or 5)-acetamido-2-methylbenziminazole forms orange-yellow needles, m. p. 235°, insoluble in boiling alcohol or cold water, soluble in about 10 parts of boiling 50% aqueous alcohol. It is readily soluble in caustic alkalis, mineral acids, and in dilute acetic acid, from which it is reprecipitated by bases (Found: N, 23.7.  $C_{10}H_{10}O_3N_4$  requires N, 23.9%).

5(or 6)-Amino-6(or 5)-acetamido-2-methylbenziminazole, obtained by reduction of the above nitro-compound with iron and boiling dilute acetic acid (see J., 1928, 174), consists of white needles, m. p. above 300°, moderately easily soluble in boiling water (Found: N, 27.8.  $C_{10}H_{12}ON_4$  requires N, 27.4%). The dihydrochloride is sparingly soluble in cold water (Found: Cl, 25.2.  $C_{10}H_{12}ON_4 \cdot 2HCl$  requires Cl, 25.6%), and the triazole (Found: N, 33.0.  $C_{10}H_9ON_5$  requires N, 32.6%) forms prisms from boiling water, not molten at 300°.

5:6-Diacetamido-2-methylbenziminazole (compare Kym and Ratner, *loc. cit.*), obtained by the action of acetic anhydride on the above amino-compound, formed colourless needles, m. p. above 300°, from boiling water (Found: N, 22.7. Calc.: N, 22.8%).

5-Nitro-1:2:4-triacetamidobenzene.—1:2:4-Triacetamidobenzene (15 g.) was mixed with potassium nitrate (6.6 g.) and added at 5–10° to sulphuric acid (75 c.c.); after remaining for 1 hour at 10°, the mixture was poured on ice, and the nitro-compound collected and washed; it crystallised from glacial acetic acid in yellow prisms (9 g.), m. p. 261°. The mother-liquor on concentration gave a further 2 g. of fairly pure nitro-compound, making the total yield 65%. This compound is sparingly soluble in hot alcohol and insoluble in water (Found: N, 19.1.  $C_{12}H_{14}O_5N_4$  requires N, 19.0%).

5-Nitro-1:2:4-triaminobenzene, obtained, together with 5(or 6)-nitro-6(or 5)-amino-2-methylbenziminazole (see Table VI, p. 1417) by hydrolysis of the triacetyl derivative, crystallised in deep red needles, m. p. 210°, from aqueous alcohol. It is insoluble in alkalis and only slightly soluble in ether.

5(or 6)-Nitro-6(or 5)-amino-2-methylbenziminazole, obtained by hydrolysis of its acetyl derivative, by the action of hydrochloric acid (Table VI) on 5-nitro-1:2:4-triacetamidobenzene, or by the action of acetic anhydride and boiling dilute mineral acids on 5-nitro-

1 : 2 : 4-triaminobenzene, crystallised in red prisms, m. p.  $292^{\circ}$ , from alcohol. It is soluble in *excess* of caustic alkalis and readily soluble in mineral acids (compare Biedermann and Ledoux, *Ber.*, 1874, 7, 1532; Nietzki and Hagenbach, *loc. cit.*) (Found : N, 28.8. Calc. : N, 29.2%). The *hydrochloride* consists of brown needles, sparingly soluble in water (Found : Cl, 15.3.  $C_6H_3O_2N_4 \cdot HCl$  requires Cl, 15.5%). The amino-group in this compound is very stable to hot concentrated aqueous alkalis.

5(or 6)-Nitro-2-methylbenziminazole (yield, 70%) was obtained from 5(or 6)-nitro-6(or 5)-amino-2-methylbenziminazole by treatment of its diazo-compound with excess of boiling alcohol.

5 : 6-Diamino-2-methylbenziminazole (Kym and Ratner, *loc. cit.*) was obtained as its *dihydrochloride* (Found : Cl, 29.9; N, 23.9.  $C_8H_{10}N_4 \cdot 2HCl$  requires Cl, 30.2; N, 23.9%) by reduction of 5(6)-nitro-6(5)-amino-2-methylbenziminazole (3 g.) with boiling 5*N*-hydrochloric acid (30 c.c.) and tin (8 g.). After removal of tin by hydrogen sulphide, the filtrate was evaporated to dryness under reduced pressure (yield, 70%). The *triazole* melted above  $300^{\circ}$  (Found : N, 40.5.  $C_8H_7N_5$  requires N, 40.5%).

5(6)-Nitro-2-methylbenziminazole-6(5)-*arsinic Acid*.—5(6)-Nitro-6(5)-amino-2-methylbenziminazole (7.5 g.) in 30 c.c. of water and 30 g. of ice with 12 c.c. of 10*N*-hydrochloric acid was diazotised at  $0^{\circ}$  with 3 g. of sodium nitrite. The diazo-solution was added at  $50^{\circ}$  to a sodium arsenite mixture prepared from arsenious oxide (5.4 g.) and sodium hydroxide (8.0 g.) in water (15 c.c.) to which 7 c.c. of 2*N*-copper sulphate solution had been added. After remaining for 30 minutes at  $60^{\circ}$ , the reaction mixture was submitted to filtration and the filtrate was acidified to litmus, again filtered, and acidified faintly to Congo-red. The *arsinic acid*, obtained in 60% yield, formed pale yellow, hexagonal plates, not molten at  $300^{\circ}$ , from glacial acetic acid, in which it was sparingly soluble (Found : As, 24.75; N, 13.7.  $C_8H_8O_5N_3As$  requires As, 24.9; N, 13.9%). The calcium and magnesium salts are amorphous but the barium salt forms fine needles. The acid can be recovered unchanged after several hours' boiling with 20% caustic alkali solution.

On reduction of the nitro-acid by freshly precipitated ferrous hydroxide at  $60^{\circ}$ , a 65% yield of 5(6)-*amino-2-methylbenziminazole-6(5)-arsinic acid* is obtained. The acid forms white needles, is amphoteric, and is remarkably stable towards boiling 5*N*-hydrochloric acid (Found : As, 27.8; N, 15.5.  $C_8H_{10}O_3N_3As$  requires As, 27.6; N, 15.5%). The *acetyl* derivative forms colourless prisms, readily soluble in alkalis and mineral acids (Found : As, 23.7; N, 13.2.  $C_{10}H_{10}O_4N_3As$  requires As, 24.0; N, 13.4%).

1 : 2 : 4 : 5-Tetra-aminobenzene tetrahydrochloride (compare

Nietzki and Hagenbach, *loc. cit.*) was obtained by reduction of 5-nitro-1:2:4-triaminobenzene with tin and boiling 5*N*-hydrochloric acid. It is sparingly soluble in cold water and on treatment of its aqueous solution with ammonia and acetic anhydride gives 1:2:4:5-tetra-acetamidobenzene (Found: N, 18.2. Calc.: N, 18.3%).

$\alpha$ -Benzbisiminazole was obtained as an amorphous white solid, not molten at 300°, when 1:2:4:5-tetra-aminobenzene hydrochloride was treated with formic acid (1 part) and 5*N*-hydrochloric acid (5 parts) for  $\frac{1}{2}$  hour at the boiling point, and the solution made alkaline with ammonia (Found: N, 35.0.  $C_8H_8N_4$  requires N, 35.4%).

$\alpha$ -2-Methylbenzbisiminazole.—5:6-Diamino-2-methylbenziminazole dihydrochloride (2 g.) was refluxed for 30 minutes with 6 c.c. of 5*N*-hydrochloric acid and 2 c.c. of formic acid; on basification with ammonia the cyclic compound was precipitated. It is an amorphous solid, not molten at 300°, readily soluble in acids but not in caustic alkali (Found: N, 32.2.  $C_9H_8N_4$  requires N, 32.6%).

$\alpha$ -2:2'-Dimethylbenzbisiminazole was obtained (a) from 5:6-diamino-2-methylbenziminazole by the action of acetic and 5*N*-hydrochloric acids, (b) by the action of boiling 5*N*-hydrochloric acid (5 parts) on 5:6-diacetamido-2-methyl- or 5(6)-amino-6(5)-acetamido-2-methyl-benziminazole, and (c) by the action of acetic anhydride (2 parts) and boiling 5*N*-hydrochloric acid (3 parts) on 1:2:4:5-tetra-aminobenzene hydrochloride. It is an amorphous white solid resembling its lower homologues in solubility, and is unmelted at 300° (Found: N, 30.3. Calc.: N, 30.1%).

4-Nitro-2-aminomethylaniline was obtained in 60% yield by reduction of 2:4-dinitromethylaniline with aqueous ammonium sulphide solution. By the action of acetic anhydride on the dry solid or of sodium acetate on an aqueous solution of its hydrochloride, was obtained 4-nitro-2-acetamidomethylaniline, which crystallised from acetone in yellow rhombs, m.p. 185° (Found: N, 20.1.  $C_9H_{11}O_3N_3$  requires N, 20.1%); no trace of 4-nitro-2-acetamidomethylacetanilide was formed even when a large excess of acetic anhydride was used. The difficulty of acetylating a methylamino-group in the *o*- or *p*-position with respect to a nitro-group is also shown in the case of 2:4-dinitromethylaniline, which cannot be acetylated with acetic anhydride even in the presence of fused sodium acetate.

*Formation of 5-Nitro-2-methylbenziminazole.*—Before the quantitative work was undertaken, it was shown that the cyclic compound was stable to 10*N*-hydrochloric acid at 160° and to boiling 50% sodium hydroxide solution, the recovery of unchanged material after many hours being almost quantitative in both cases.

*General method of estimation.* Aliquot portions of the reaction

mixture were withdrawn after various times, cooled rapidly, and treated with sodium acetate. The solids obtained were digested with excess of 2*N*-caustic soda, and the nitro-diamine collected. The filtrate was acidified with acetic acid, and the cyclic compound filtered off. The combined mother-liquors were evaporated to dryness, and the residual solids extracted with acetone. The substance obtained by evaporation of the acetone was redigested with caustic alkali and separated into the same two compounds.

TABLE I.—*Formation of 5-nitro-2-methylbenziminazole from 4-nitro-1:2-diaminobenzene, acetic anhydride (1 part), and hydrochloric acid (5 parts) at the boiling point.*

Time (mins.).	2 <i>N</i> -HCl.		4 <i>N</i> -HCl.		10 <i>N</i> -HCl.	
	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.
15	40	54	38	50	42	48
30	24	67	20	62	27	60
45	13	70	11	77	14	75
60	5	75	5	82	5	80
75	trace	85	trace	85	trace	86
90	nil	86	nil	85	nil	85

TABLE II.—*Formation of 5-nitro-2-methylbenziminazole from 4-nitro-1:2-diacetamidobenzene and hydrochloric acid (5 parts) at the boiling point.* The method of estimation was as before, except that in the cases marked (a) the unchanged material was removed by filtration after cooling and weighed and the estimation was performed on the filtrate. In the following tables, (a) has this significance and (b) indicates complete hydrolysis as shown by complete solution.

Time (mins.).	2 <i>N</i> -HCl.		4 <i>N</i> -HCl.		10 <i>N</i> -HCl.	
	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.
5	—	—	—	—	29 (b)	60 (b)
7	—	—	† 6 (a)	14 (a)	—	—
10	—	—	† 19 (a)	30 (a)	—	—
15	—	—	23 (b)	64 (b)	19	70
18	* 11 (a)	22 (a)	—	—	—	—
30	27 (b)	67 (b)	11	80	8	80
45	20	72	6	90	4	90
60	10	80	1	92	nil	93
75	5	87	nil	94	—	—
90	nil	90	—	—	—	—

Unchanged material: \*55%, †75%, ‡42%.

TABLE III.—*Formation of 5-nitro-2-methylbenziminazole from 4-nitro-1:2-diacetamidobenzene and 25% caustic alkali solution.*

Time (mins.) .....	5	30	60	180
% Nitro-diamine .....	4	5	6	4
% Ring compound .....	82	85	78	83

TABLE IV.—*Formation of 5-nitro-2-methylbenziminazole from 4- and 5-nitro-2-aminoacetanilide and 4N-hydrochloric acid (5 parts) at the boiling point.* Owing to the sparing solubility in cold mineral acids of these two bases, it was found possible approximately to estimate the amounts of unchanged material after limited action of the mineral acid (a) by a method analogous to that employed for the acid hydrolysis of 4-nitro-1:2-diacetamidobenzene.

Time (mins.).	From 4-nitro-compound.		From 5-nitro-compound.	
	% Nitro-diamine.	% Ring compound.	% Nitro-diamine.	% Ring compound.
1	*19 (a)	47 (a)	†22 (a)	50 (a)
5	32 (b)	51 (b)	30 (b)	60 (b)
15	10	84	12	72
30	—	—	4	79
60	nil	92	nil	83

Unchanged material : \*24%, †20%.

TABLE V.—*Formation of 5-nitro-2-methylbenziminazole and of 4-nitro-1:2-diaminobenzene from 4-nitro-1:2-diacetamidobenzene and 20% methyl-alcoholic hydrogen chloride (5 parts).* The nitro-diamine and acetic acid do not react in the presence of methyl-alcoholic hydrogen chloride, methyl acetate being formed.

At the boiling point (atmospheric pressure).			
Time (mins.).	% Unchanged.	% Nitro-diamine.	% Ring compound.
(a) 10	58	15	17
(b) 30	—	38	47
60	—	35	50
180	—	40	52

At 160°. 4-Nitro-1:2-diacetamidobenzene (2 g.) was heated in a sealed tube for 3 hours at 160° with 20% methyl-alcoholic hydrogen chloride (10 c.c.); on dilution with water (20 c.c.) and basification with dilute caustic soda solution, 1.2 g. (96%) of 4-nitro-1:2-diaminobenzene were obtained. No trace of the cyclic compound was found in the acidified filtrate.

TABLE VI.—*Formation of 5(6)-nitro-6(5)-amino-2-methylbenziminazole from 5-nitro-1:2:4-triacetamidobenzene and hydrochloric acid (5 parts) at the boiling point.*

Time (mins.).	2N-HCl.		4N-HCl.		20% Methyl-alcoholic hydrogen chloride.	
	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.	% Nitro-diamine.	% Ring compd.
2	—	—	*10 (a)	42 (a)	—	—
5	—	—	—	—	†12 (a)	52 (a)
6	—	—	23 (b)	67 (b)	—	—
12	20 (b)	64 (b)	—	—	—	—
15	—	—	8	83	15 (b)	80 (b)
30	8	79	trace	89	17	78
60	(nil)	87	nil	91	15	80

Unchanged material : \*40%, †20%.

*Formation of Benziminazole and of 2-Methylbenziminazole from o-Phenylenediamine, Formic Acid (1 part) or Acetic An-*

hydride (1 part), and 4*N*-Hydrochloric Acid (5 parts) at the Boiling Point.—Aliquot portions of the reaction mixture were periodically withdrawn, rapidly cooled, and treated with sodium nitrite; the triazole corresponding to the unchanged diamine was then precipitated. The filtrate from the triazole on basification with dilute aqueous ammonia gave the cyclic compound; a further quantity was obtained by concentration of the filtrate.

TABLE VII.

Time (mins.).	<i>Benziminazole.</i>		<i>2-Methylbenziminazole.</i>	
	% Diamine.	% Ring compound.	% Diamine.	% Ring compound.
5	39	55	45	50
15	12	80	20	70
30	nil	95	nil	87

*Formation of 2-Methylbenziminazole from Diacetyl-o-phenylenediamine and Hydrochloric Acid (5 parts) or Caustic Alkali at the Boiling Point.*—When 2*N*- or 4*N*-acid had been used, examination of the solution for diamine (or *o*-aminoacetanilide) by means of nitrous acid gave, even after short periods of treatment, traces only of the triazole and more than 80% yields of the ring compound. The use of 25% caustic alkali solution gave similar results.

*Formation of NN'-Dimethyl-o-phenylenediamine.*—Diacetyl-o-phenylenediamine (2 g.) was heated at 160° for 3 hours in a sealed tube with 20% methyl-alcoholic hydrogen chloride (10 c.c.). The blue solution was basified; extraction with ether and removal of the solvent gave 0.4 g. of *NN'*-dimethyl-o-phenylenediamine, m. p. 34° after crystallisation from acetone. No cyclic compound could be isolated.

*Formation of 5-Nitro-1:2-dimethylbenziminazole.*—The separation of amine from ring compound recorded below was done by fractional crystallisation from alcohol.

TABLE VIII.

<i>Formation from 4-nitro-2-aminomethylaniline, acetic anhydride (1 part) and 4<i>N</i>-hydrochloric acid at the boiling point.</i>			<i>Formation from 4-nitro-2-acetamidomethylaniline and 4<i>N</i>-hydrochloric acid at the boiling point.</i>	
Time (mins.).	Amine.	% Ring compound.	Amine.	% Ring compound.
5	Present, not estimated	71	—	—
15	—	—	Present, not estimated	60
30	Present, not estimated	60	” ”	64
45	Trace	70	Trace	78
60	Nil	85	Nil	



*Formation of 5-Nitro-1:2-dimethylbenziminazole from 4-Nitro-2-acetamidomethylaniline and Methyl-alcoholic Hydrogen Chloride at the Boiling Point.*—4-Nitro-2-acetamidomethylaniline (5 g.) and 20% methyl-alcoholic hydrogen chloride (25 c.c.) were boiled under reflux for 1 hour and the mixture was evaporated to dryness. The residue, dissolved in water (10 c.c.) and filtered, was basified with ammonia and the bases (3.1 g.; 70%) were fractionated from 70% alcohol, giving 1.8 g. (40%) of 5-nitro-1:2-dimethylbenziminazole and 0.4 g. (12%) of 4-nitro-2-aminomethylaniline.

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## CLXXXIV.—*The Sulphonation of m-Chlorophenol and Some New Halogenophenols.*

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THE monosulphonation of *m*-chlorophenol, whether hot or cold, gives almost entirely 3-chlorophenol-6-sulphonic acid. On the current electronic theory this result was to be anticipated, since the normally less intensely activated 4-position is deactivated by the general effect of the 3-chloro-substituent (compare Hodgson and Jenkinson, J., 1929, 469). With the more powerful kationoid reagent, oleum, disulphonation takes place in the 4- and 6-positions.

The solubilities of the salts of 3-chlorophenol-6-sulphonic acid resemble those of the corresponding sulphates, *viz.*,  $\text{Ca} > \text{Sr} > \text{Ba}$ , and  $\text{Na} > \text{K}$ , and the calcium salt is unique in forming a hydrate.

The tetrahydrated barium salts of the 4:6-disulphonic acid and of its 2-halogeno-derivatives are of interest from the co-ordination standpoint, and it is suggested that two of the molecules of water are co-ordinated with the barium atom by means of oxygen atoms and that each sulphonic acid group is co-ordinated by means of its negatively charged oxygen atoms with the hydrogen atoms of a molecule of water (compare Sidgwick, "Electronic Theory of Valency," 1927, pp. 192 and 195).

3-Chloro-2:4-dibromo-6-nitrophenol is obtained in two crystalline forms according to the method of preparation, *viz.*, elongated needles by the dibromination of 6-nitro-3-chlorophenol, and stout prisms by the nitration of 3-chloro-2:4-dibromophenol. Though interconvertible, each form could be recrystallised from alcohol without change of habit. It is tentatively suggested that the two forms are an example of Kekulé's ortho-isomerism.

## EXPERIMENTAL.

*Monosulphonation of 3-Chlorophenol at 100° and at the Ordinary Temperature.*—3-Chlorophenol (12 g.) and concentrated sulphuric acid (20 g.) were heated together for 8 hours on the water-bath, the mixture was then poured into water (1000 c.c.), and the solution was heated on the water-bath while it was being made neutral to Congo-red by addition of barium carbonate. The residue after filtration was extracted several times with boiling water (1000 c.c. in all) and the solution obtained, combined with the filtrate above, was evaporated to dryness, leaving the barium salt (26 g.) of the sulphonic acid (yield, theoretical). The salt was decomposed by dilute sulphuric acid, the solution evaporated to small bulk, and the remainder of the water removed in a vacuum desiccator containing calcium chloride; colourless prisms of 3-chlorophenol-6-sulphonic acid were obtained containing a variable quantity of water of hydration. The constitution of the acid has already been deduced by the authors (J., 1929, 2923). The same results were also obtained when the sulphonation was conducted at room temperature.

The following salts are prepared by adding the corresponding carbonates to solutions of the acid until these are neutral to Congo-red: The *potassium* salt forms anhydrous prisms (Found: C, 28.9; H, 1.7; Cl, 14.4; K, 16.0.  $C_6H_4O_4ClSK$  requires C, 29.2; H, 1.7; Cl, 14.4; K, 15.9%). The *sodium* salt is much more soluble in water than the potassium salt, and separates from this solvent in anhydrous, minute, elongated prisms (Found: Cl, 15.6; Na, 10.2.  $C_6H_4O_4ClSNa$  requires Cl, 15.4; Na, 10.0%). The *ammonium* salt crystallises in large stout prisms (Found: Cl, 15.9; S, 14.5.  $C_6H_4O_4ClSNH_4$  requires Cl, 15.7; S, 14.2%). The *barium* salt forms anhydrous, short, stout prisms which are sparingly soluble in water [Found: C, 26.2; H, 1.6; Ba, 24.6.  $(C_6H_4O_4ClS)_2Ba$  requires C, 26.1; H, 1.4; Ba, 24.8%]. The *strontium* salt separates from water, in which it is more soluble than the barium salt, in anhydrous flat prisms [Found: Sr, 17.1.  $(C_6H_4O_4ClS)_2Sr$  requires Sr, 17.3%. 0.2195 G. gave 0.3339 g. of mixed silver chloride and strontium sulphate; required, 0.3291 g.). The *lead* salt crystallises in anhydrous prisms which are easily soluble in water [0.2490 g. gave 0.2991 g. of mixed precipitates (see below); required, 0.3016 g.]. The monohydrated *calcium* salt separates from water, in which it is readily soluble, in flat rectangular prisms [Found: C, 30.0; H, 2.4; Cl, 15.0; Ca, 8.6.  $(C_6H_4O_4ClS)_2Ca \cdot H_2O$  requires C, 30.4; H, 2.1; Cl, 15.0; Ca, 8.5%].

*Analytical Note.*—The above salts were analysed for carbon and hydrogen by admixture with lead chromate and combustion in a stream of oxygen in a tube packed with lead chromate. Very few

gave stoicheiometric results, but those obtained are recorded. In other cases the amounts of mixed silver halides and insoluble sulphates obtained by the Carius method are given, and also the percentage of metal estimated as sulphate.

*Halogenation of 3-Chlorophenol-6-sulphonic Acid.*—(a) *Dichlorination.* Barium 3-chlorophenol-6-sulphonate (14 g.) was dissolved in water (1000 c.c.), and the theoretical amount of a freshly prepared solution of barium hypochlorite added. After 12 hours, the mixture was neutralised with sulphuric acid, and the filtered liquid evaporated to small bulk; *barium 2 : 3 : 4-trichlorophenol-6-sulphonate* then separated in good yield as flat rhombs sparingly soluble in water [Found: Ba, 20.1.  $(C_6H_2O_4Cl_3S)_2Ba$  requires Ba, 20.2%]. The *dihydrate* of this salt separated on one occasion in very long prisms [Found: Ba, 19.25.  $(C_6H_2O_4Cl_3S)_2Ba \cdot 2H_2O$  requires Ba, 19.0%. 0.1225 G. gave 0.1849 g. of mixed precipitates (see above); required, 0.1849 g.].

*2 : 3 : 4-Trichlorophenol* is obtained by heating the above salt in aqueous sulphuric acid (80%) during the passage of steam, in which it is volatile; it crystallises from light petroleum in elongated needle-like prisms, m. p. 79° (Found: Cl, 53.7.  $C_6H_3OCl_3$  requires Cl, 53.9%).

*2 : 3 : 4-Trichloroanisole*, obtained from the phenol by the action of methyl sulphate and sodium hydroxide solution, crystallises from alcohol in long, flat, rectangular prisms, m. p. 69.5° (Found: Cl, 50.3.  $C_7H_5OCl_3$  requires Cl, 50.3%).

(b) *Dibromination.* Barium 3-chloro-2 : 4-dibromo-6-sulphonate *dihydrate* was obtained by the action of bromine (2.5 c.c.; 8 g.) on barium 3-chlorophenol-6-sulphonate (7 g.) dissolved in water (500 c.c.). The solution obtained was made neutral to Congo-red with barium carbonate, filtered, and evaporated to small bulk; the product then crystallised in very long prisms sparingly soluble in water [Found: Ba, 15.1.  $(C_6H_2O_4ClBr_2S)_2Ba \cdot 2H_2O$  requires Ba, 15.2%. 0.1225 G. gave 0.2260 g. of mixed precipitates; required, 0.2338 g.].

The *potassium* salt separates from water, in which it is sparingly soluble, in anhydrous, thin, flat plates (Found: C, 17.8.  $C_6H_2O_4ClBr_2SK$  requires C, 17.8%. 0.1116 G. gave 0.1430 g. of mixed silver halides; required, 0.1432 g.).

The *sodium* salt was obtained in clusters of anhydrous flat plates (Found: Na, 6.0.  $C_6H_2O_4ClBr_2SNa$  requires Na, 5.9%. 0.2542 G. gave 0.3400 g. of mixed silver halides; required, 0.3320 g.).

The above salts are extremely stable and very difficult to hydrolyse, as they crystallise unchanged from hot concentrated sulphuric acid; the free acid, however, is easily hydrolysed under the same conditions.

*3-Chloro-2 : 4-dibromophenol* was prepared by heating for 8 hours on the water-bath a mixture of 3-chlorophenol (65 g.) and concentrated sulphuric acid (12 g.), then pouring it on ice (30 g.) and adding bromine (16 g.). After 4 hours, a small quantity (less than 1 g.) of 3-chloro-2 : 4 : 6-tribromophenol which had separated was removed and the filtrate was hydrolysed in steam; the 3-chloro-2 : 4-dibromophenol (9.5 g.) which passed over crystallised from light petroleum in long colourless prisms, m. p.  $88^{\circ}$  (0.2228 g. gave 0.4062 g. of mixed silver halides; required, 0.4039 g.). Its constitution was established by nitration to *3-chloro-2 : 4-dibromo-6-nitrophenol* as follows: the phenol (9 g.), dissolved in glacial acetic acid (20 c.c.), was treated gradually, whilst ice-cold, with a solution of nitric acid (1.8 c.c.;  $d$  1.5) in glacial acetic acid (7 c.c.). The mixture was kept over-night and the 3-chloro-2 : 4-dibromo-6-nitrophenol was then precipitated by the addition of water (500 c.c.), and crystallised from alcohol (yield, 8.0 g.; 76%); m. p.  $90^{\circ}$  (0.2143 g. gave 0.3470 g. of mixed silver halides; required, 0.3504 g.). The product was identical (m. p. and mixed m. p.) with that obtained by treating 3-chloro-6-nitrophenol (3 g.), dissolved in glacial acetic acid (15 c.c.), with bromine (2.4 g.).

*3-Chloro-2 : 4-dibromoanisole*, prepared by the usual method, crystallises from alcohol in very long, flat prisms, m. p.  $92^{\circ}$  (0.2312 g. gave 0.4019 g. of mixed silver halides; required, 0.3996 g.).

*3-Chloro-2 : 4 : 6-tribromoanisole* is obtained by bromination of the previous product in glacial acetic acid, and also by methylation of the corresponding phenol (see above). It crystallises from alcohol or acetic acid in long needles, m. p.  $92^{\circ}$  (0.1409 g. gave 0.2643 g. of mixed silver halides; required, 0.2620 g.).

(c) *Di-iodination.* *3-Chloro-2 : 4-di-iodophenol-6-sulphonic acid trihydrate* is obtained from the corresponding barium salt (see below) by treatment with dilute sulphuric acid, the solution being then evaporated to small bulk and the acid precipitated by means of concentrated hydrochloric acid; it forms long flat prisms, m. p.  $167^{\circ}$  (slight decomp.) (Found: S, 6.7.  $C_6H_3O_4ClI_2S \cdot 3H_2O$  requires S, 6.2%. 0.2328 G. gave 0.2764 g. of mixed silver halides; required, 0.2774 g.).

The tetrahydrated *barium* salt was obtained when barium 3-chlorophenol-6-sulphonate (10 g.), powdered iodine (20 g.), precipitated mercuric oxide (8 g.), alcohol (60 c.c.), and water (20 c.c.) were shaken together for 30 minutes. After removal of the excess iodine by the gradual addition of sodium bisulphite solution, the whole mixture was evaporated to dryness, the residue extracted with boiling water (300 c.c.), and barium chloride (2 g.) added to the filtered extract; when this was then evaporated to 100 c.c., the sparingly soluble salt was obtained in long thin prisms. Any mercuric iodide which

separate with the product may be removed by extraction with boiling alcohol [Found: Ba, 12.1. ( $\text{C}_6\text{H}_2\text{O}_4\text{ClI}_2\text{S}$ )<sub>2</sub>.Ba, 4H<sub>2</sub>O requires Ba, 12.17%]. (Mercuric iodide is definitely soluble in hot water, and may be steam-distilled from hot sulphuric acid, passing over in the yellow form which subsequently becomes red.)

*3-Chloro-2:4-di-iodophenol*, obtained from its 6-sulphonic acid (above) by hydrolysis, crystallises from light petroleum in long prisms, m. p. 111.5° (0.1329 g. gave 0.2161 g. of mixed silver halides; required, 0.2144 g.).

*3-Chloro-2:4-di-iodoanisole*, readily obtained in the usual way, crystallises from alcohol in somewhat stout prisms, m. p. 105° (0.1715 g. gave 0.2701 g. of mixed silver halides; required, 0.2667 g.).

*Disulphonation of 3-Chlorophenol*.—*Barium 3-chlorophenol-4:6-disulphonate tetrahydrate* is obtained when 3-chlorophenol (12.8 g.) is added gradually to oleum (75 g.; 27% SO<sub>3</sub>) with cooling, the mixture kept over-night, then heated for 2 hours on the water-bath, poured into water (1000 c.c.), rendered neutral to Congo-red by addition of barium carbonate (about 10 g.), and the filtered solution evaporated to dryness. It is a white powder, which, like the salts of the other sulphonic acids described later, is very soluble in water, in marked contrast to the sparing solubility of the barium salts of the 6-monosulphonic acids described above. The product crystallises from water in clusters of minute short prisms (Found: Ba, 27.4.  $\text{C}_6\text{H}_3\text{O}_7\text{ClS}_2\text{Ba}, 4\text{H}_2\text{O}$  requires Ba, 27.7%).

*Halogenation of the above Barium Salt and Preparation of the 2-Halogeno-3-chlorophenols*.—(a) *Chlorination*. *Barium 2:3-dichlorophenol-4:6-disulphonate tetrahydrate* is obtained when the foregoing barium salt (24 g.), dissolved in water (500 c.c.), is treated with the theoretical quantity of freshly prepared barium hypochlorite solution, the mixture kept over-night and neutralised with sulphuric acid, and the solution filtered and evaporated to dryness. It crystallises from water in clusters of long prisms (Found: Ba, 26.2.  $\text{C}_6\text{H}_2\text{O}_7\text{Cl}_2\text{S}_2\text{Ba}, 4\text{H}_2\text{O}$  requires Ba, 25.9%).

*2:3-Dichlorophenol*, prepared from the above product in 70% yield by the usual procedure for the elimination of sulphonic acid groups, forms a mass of prisms on solidification after distillation, m. p. 58°, b. p. 206° (Found: Cl, 43.5. Calc.: Cl, 43.6%).

*2:3-Dichloro-4:6-dibromophenol* is readily obtained by direct dibromination of the above phenol and separates from glacial acetic acid in colourless needles which rapidly become opaque; m. p. 90° (0.1581 g. gave 0.3230 g. of mixed silver halides; required, 0.3266 g.).

*2:3-Dichloro-4:6-dibromoanisole* crystallises from alcohol in long needle-like prisms, m. p. 82° (0.1324 g. gave 0.2623 g. of mixed silver halides; required, 0.2621 g.).

(b) *Bromination*. 3-Chlorophenol (12.8 g.) was disulphonated as above, the solution diluted with water (100 c.c.) and treated with bromine (16 g.), and the resulting solution hydrolysed to give the corresponding phenol or diluted to 1000 c.c. and neutralised with barium carbonate, etc., as above.

*Barium 3-chloro-2-bromophenol-4 : 6-disulphonate tetrahydrate* crystallises from water in small prisms (Found: Ba, 24.0.  $C_6H_2O_7ClBrS_2Ba \cdot 4H_2O$  requires Ba, 23.8%. 0.1615 G. gave 0.1541 g. of mixed precipitates; required, 0.1558 g.).

3-Chloro-2-bromophenol is obtained in 75% yield as above and crystallises from light petroleum in large stout prisms, m. p. 55.5°, b. p. 225° (0.2438 g. gave 0.3892 g. of mixed silver halides; required, 0.3910 g.).

3-Chloro-2-bromoanisole, obtained by the action of methyl sulphate and sodium hydroxide on the above phenol, crystallises from alcohol in long colourless plates, m. p. and mixed m. p. with a specimen prepared from 3-chloro-2-aminoanisole (Hodgson and Kershaw, *loc. cit.*), 50°.

A solution of 3-chloro-2-bromophenol (7 g.) in ice-cold glacial acetic acid (7 c.c.) was treated with nitric acid (3.5 c.c.; *d* 1.5) in glacial acetic acid (4 c.c.). After 12 hours, steam distillation removed the volatile 3-chloro-2-bromo-6-nitrophenol, which crystallised from light petroleum in small yellow prisms, m. p. 98.5° (0.0755 g. gave 0.0990 g. of mixed silver halides; required, 0.0991 g.), leaving behind the non-volatile 3-chloro-2-bromo-4-nitrophenol, which crystallised from dilute alcohol in fine, almost colourless, needles, m. p. 136° (0.1949 g. gave 0.2601 g. of mixed silver halides; required, 0.2569 g.).

(c) *Iodination*. *Barium 3-chloro-2-iodophenol-4 : 6-disulphonate tetrahydrate* was prepared by stirring for 1 hour a mixture of barium 3-chlorophenol-4 : 6-disulphonate (13 g.), finely powdered iodine (7.6 g.), precipitated mercuric oxide (3.3 g.), alcohol (50 c.c.), and water (50 c.c.), during which period most of the iodine disappeared. The alcohol was then boiled off, and the residue extracted with boiling water (200 c.c.); the filtered extract on slow evaporation gave the product in small rectangular prisms (Found: Ba, 22.4.  $C_6H_2O_7ClIS_2Ba \cdot 4H_2O$  requires Ba, 22.1%. 0.1814 G. gave 0.1745 g. of mixed precipitates; required, 0.1783 g.).

3-Chloro-2-iodophenol was prepared by hydrolysis of the above disulphonate and also by the action of potassium iodide on diazotised 3-chloro-2-aminophenol. It crystallises from light petroleum in colourless needles, m. p. 56° (Found: 0.1107 g. gave 0.1692 g. of mixed silver halides, required, 0.1646 g.).

*Colour Reactions of the Sulphonic Acids with Ferric Chloride.*—An aqueous solution of 3-chlorophenol-6-sulphonic acid gives a violet

colour with ferric chloride, and the salts give similar but deeper colours. The colours are not produced in concentrated acid solutions.

The halogeno-derivatives of the above acid give bluer colours than the parent acid, all the halogens having approximately the same effect: the nitro-derivatives give brownish-red colours.

3-Chlorophenol-4:6-disulphonic acid and its salts give red colours: the halogeno- and nitro-derivatives have similar effects on the shades as in the case of the monosulphonic acids and salts.

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## CLXXXV.—*A General (Exact) Equation to the Potentiometric-titration Curve.*

By BERNARD CAVANAGH.

### *Section 1.*

IN a previous paper (Part II; J., 1928, 855) an exact equation was obtained, on thermodynamic grounds, representing the whole potentiometric-titration curve in all cases where (a) the analytical reaction consists in the combination of two ions of like valency to form a substance of constant activity such as a precipitate, and (b) the indicator electrode behaves as a "soluble electrode" towards either of these ions. Essentially of the tractable form,

$$X = \sinh U \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(where  $U$  and  $X$  represent distance from the equivalence point in terms of potential and of quantity of reagent, respectively), this equation was used in developing certain highly refined methods of titration. It will now be shown that both the equation and the methods arising out of it can be generalised. A system involving both analytical and electrode reactions of the most general type yields, under equilibrium conditions, a titration curve exactly represented by an equation of the form

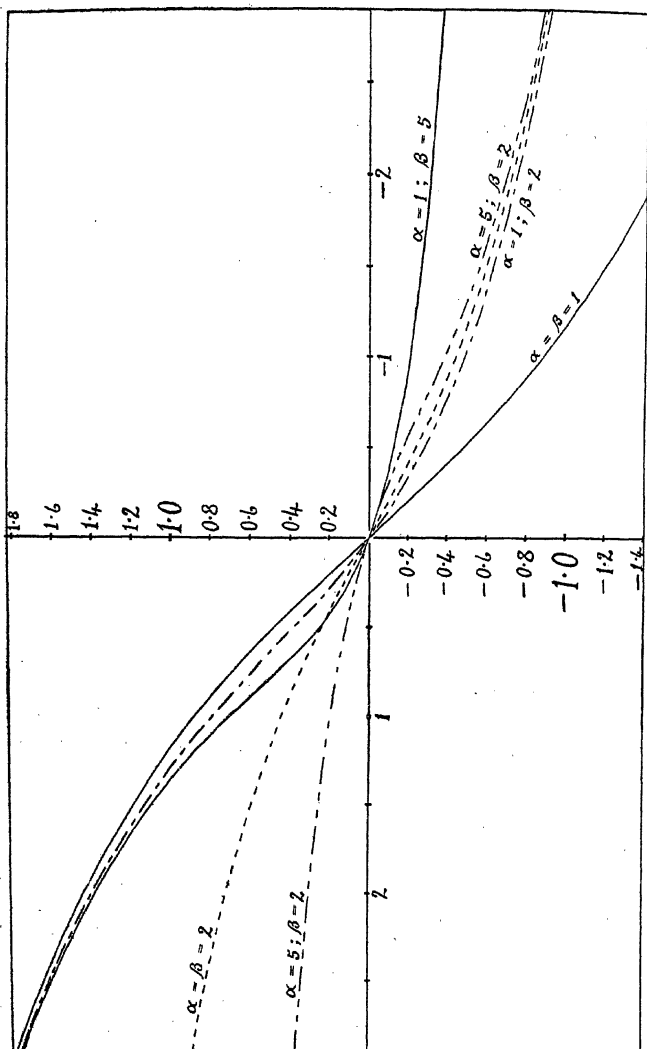
$$X = \sinh_{\alpha\beta} U \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

$$\sinh_{\alpha\beta} U = \frac{1}{2}(e^{\alpha U} - e^{-\beta U}) \quad . \quad . \quad . \quad . \quad . \quad (3)^*$$

\* This equation could be written in the form  $\sinh U = e^{\frac{\alpha-\beta}{2}U} \sinh \frac{\alpha+\beta}{2}U$ , and similarly for other hyperbolic functions of  $U$ , but the formulæ would be, not only cumbersome, but less direct in their physicochemical significance.

Fig. 1.  
Typical forms of the curve represented by the general titration-curve equation. (Graphs of the function  $X = \frac{\sinh U}{\alpha\beta}$  for various assigned values of the parameters  $\alpha$  and  $\beta$ .)



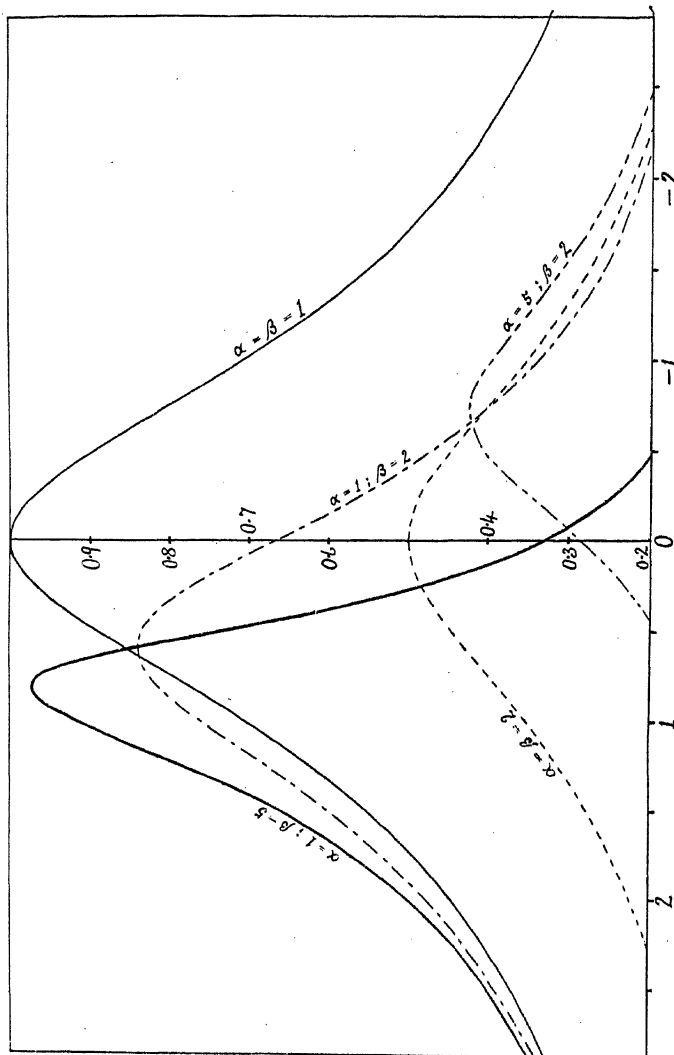
The origin represents the point of exact equivalence. Abscissae ( $X$ ) represent distance from the equivalence point in terms of quantity of reagent solution, the unit being  $H$  c.c. (see Section 2). Ordinates ( $U$ ) represent distance from the equivalence point in terms of potential, the unit being  $RT/F$  (i.e., about 25 millivolts). Three kinds of broken line are used to distinguish the curves.

and  $\alpha$  and  $\beta$  are two simple numbers characteristic of the system (see Section 3; and Fig. 1).

Between the function defined in (3) and the corresponding cosine and other functions (see Section 4) many of the inter-relations of the ordinary hyperbolic functions hold good (for fixed values of  $\alpha$  and  $\beta$ ), while others assume a more general form. These relations facilitate the derivation of methods of refined titration essentially



FIG. 2.  
 Derived curves, corresponding with those of Fig. 1. [*Graphs of the function*  $h^{-1} \operatorname{sech} \frac{g}{\alpha\beta}$  ( $g + \operatorname{arcsinh} X$ ), i.e., of  $h^{-1} \operatorname{sech} (g + U)$ .]



Abscissae ( $X$ ) correspond exactly with those of Fig. 1. Ordinates represent rate of change of potential,  $dU/dX$  (i.e., the slope of the corresponding curve in Fig. 1), the unit being  $RT/FH$ , or about  $25/H$  millivolts/c.c.

similar to those already described, but with the advantage of general applicability.

By means of these methods, not only is the sensitivity, or absolute precision, obtainable from the accepted reactions very much increased, but also other reactions should become available for analytical purposes which otherwise would not be sufficiently sensitive. Incidentally the same methods also provide an accurate

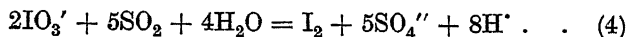
means of determining equivalence-point potentials and reaction constants (compare Part II, p. 870).

The rigorous deduction of the general titration-curve equation appears to be especially useful in providing a sound basis for the quantitative study of all the various analytical and electrode reactions that are now available or may yet be discovered. In so far as such study is to be anything more than mere empiricism, it must rest upon the assumption and the attempted realisation of equilibrium conditions, and this is the only assumption on which the following deduction is based.

### *Section 2. Deduction of the Equation.*

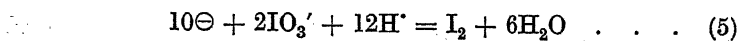
This deduction may be effected concisely and yet with strict generality by adopting the device of writing the chemical and thermodynamic equations in an algebraic manner, such that no formal distinction need be made between products of the reactions and reactants other than the two principal reactants. Four abstract or typical molecular symbols will then suffice to represent all possibilities, whereas otherwise eight at least would be necessary. The procedure at this stage may be illustrated by a concrete case.

The reduction of iodate ion by (aqueous) sulphur dioxide in strongly acid solution has recently been studied potentiometrically (Hendrixson, *J. Amer. Chem. Soc.*, 1925, 47, 1319; the author actually used a solution of sodium sulphite, but in effect this was the same as adding aqueous sulphur dioxide, since a large excess of acid was present), and shown to proceed in two clearly separated stages. Considering only the first of these, the analytical reaction is

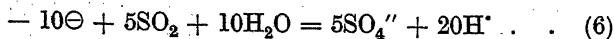


Iodate ion and sulphur dioxide are the two principal reactants; the latter, being the added substance, may conveniently be called the "reagent," and the former the "titrated substance." In order to avoid needless repetition, the word "substance" will be taken to include ionic or molecular species throughout this paper, and similarly the expression "g.-mol." will cover "g.-ion."

Before the first addition of reagent, the only electrode reaction is

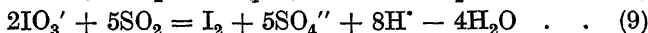
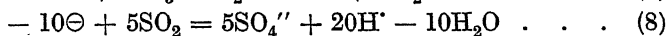
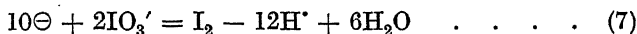


(where the symbol  $\ominus$  represents one faraday of negative electricity), but when once the titration has commenced there is the alternative electrode reaction



obtained by subtracting (5) from (4). These equations must now

be re-written in the algebraic manner convenient for the present purpose by transferring the symbols of the "subsidiary reactants," *i.e.*, all save the two principal reactants, to the right-hand sides with change of sign, thus:



and the corresponding thermodynamic equations (for equilibrium) can be written logarithmically in an entirely parallel manner, the algebraic signs being retained.

We now revert to the general treatment. Representing the molecular or ionic symbols (in the abstract) by capital letters, and taking A as the titrated substance, and B as the reagent, we express the alternative electrode reactions quite generally by the equations

$$\pm \nu \ominus + aA = \Sigma pP \quad . \quad . \quad . \quad (10)$$

$$\mp \nu \ominus + bB = \Sigma qQ \quad . \quad . \quad . \quad (11)$$

the small letters representing numerical coefficients, of which those on the right, typified by  $p$  and  $q$ , may be either positive or negative as in equations (7) and (8). From the latter it is also seen that the symbols represented by P, Q, etc., are not necessarily all different. The equation for the analytical reaction is obtained from (10) and (11) by addition, giving

$$aA + bB = \Sigma pP + \Sigma qQ \quad . \quad . \quad . \quad (12)$$

and the three thermodynamic equations corresponding to (10), (11), (12), respectively, are then written in terms of the equivalent concentrations  $C_A$ ,  $C_B$ , etc., the activity coefficients  $\gamma_A$ ,  $\gamma_B$ , etc., and the measured potential  $E$ . It is convenient to adopt the convention that the direction in which  $E$  changes during titration is taken as the negative direction, thus avoiding alternative signs, and we have

$$\nu F/RT \cdot (E_0 - E) + a \log C_A \gamma_A = \Sigma p \log C_P \gamma_P \quad . \quad . \quad (13)$$

$$- \nu F/RT \cdot (E'_0 - E) + b \log C_B \gamma_B = \Sigma q \log C_Q \gamma_Q \quad . \quad . \quad (14)$$

$$- \log K + a \log C_A \gamma_A + b \log C_B \gamma_B = \Sigma p \log C_P \gamma_P + \Sigma q \log C_Q \gamma_Q \quad . \quad . \quad (15)$$

in which logarithms (as throughout this paper) are to the base  $e$ ;  $F$ ,  $R$ , and  $T$  have their usual significance; and the three constants,  $E_0$ ,  $E'_0$ , and  $K$ , are connected by the relation

$$\log K = \nu F/RT \cdot (E'_0 - E_0) \quad . \quad . \quad . \quad (16)$$

These equations express the assumption of equilibrium conditions.

Now suppose (as in Part I, J., 1928, 843, and Part II, *loc. cit.*) that at any given stage of the titration,  $M$  c.c. of the reagent solution are

still required in order to reach the exact equivalence point. Thus  $M$  may be positive or negative, but in any case, to know  $M$  is, from the experimental point of view, to know the result of the titration. If  $n$  is the normality of the reagent solution (which may or may not be known) then the excess of the titrated substance at this stage is evidently  $Mn$  mg.-equivs.\*

In order to show how adsorption by precipitates (if any) would affect the titration curve, a coefficient,  $\theta_A$ , is now introduced, representing the ratio of the amount of A present in solution (*i.e.*, not adsorbed) to the total amount present (compare Part I, p. 848); a similar coefficient,  $\theta_B$ , relates to B.

Then if  $V$  c.c. is the volume of the solution at this stage, the total amount (mg.-equivs.) of A in the vessel is  $VC_A/\theta_A$ , and similarly that of B is  $VC_B/\theta_B$ , and since the excess of A is  $Mn$  mg.-equivs.,

$$Mn = VC_A/\theta_A - VC_B/\theta_B \quad (17)$$

The remaining steps, by which  $C_A$  and  $C_B$  are eliminated and the result is reduced to a tractable form, will be plain if three constants  $\alpha$ ,  $\beta$ ,  $\bar{E}_0$ , and two other quantities,  $H$  and  $G$  (not in general constant, but independent of  $C_A$  and  $C_B$ ), are first defined by the equations

$$\alpha\alpha = \beta\beta = \nu$$

$$(\alpha + \beta)\bar{E}_0 = \alpha E'_0 + \beta E'_0 \quad (18)$$

$$(\alpha + \beta)G = \log(\gamma_B\theta_B/\gamma_A\theta_A) + \sum \frac{p}{a} \log C_F\gamma_F - \sum \frac{q}{b} \log C_Q\gamma_Q \quad (19)$$

$$(a + b) \log(nH/2V) = \log K - a \log \gamma_A\theta_A - b \log \gamma_B\theta_B + \sum p \log C_F\gamma_F + \sum q \log C_Q\gamma_Q \quad (20)$$

Then, from equations (13), (14), (15), and (17), the general titration-curve equation connecting  $M$  and  $E$  is obtained in the form

$$M/H = \sinh_{\alpha\beta}[(F/RT)(E - \bar{E}_0) + G] \quad (21)$$

and, since this is identical with equation (2),

$$X = M/H \quad (22)$$

$$U = (F/RT) \cdot (E - \bar{E}_0) + G \quad (23)$$

From equations (19) and (20),  $G$  and  $H$  are seen to depend on the concentrations of the products and subsidiary reactants (if any), the adsorption and activity coefficients, and (in the case of  $H$ ) the volume of the solution. Their complexity and probable variation might appear, at first sight, to render impracticable the general

\* Ordinary usages have been adhered to as far as possible, but it is plain that the reagent might be measured in other units—in g. of solution, or of the pure substance B, or of some compound of B, etc.—so long as  $n$  is defined as the number of mg.-equivs. of B per unit.

application of the equation and of the methods of titration based upon it, but this is not the case. In using these methods, variation in  $H$  and  $G$  can be accurately allowed for by applying a predetermined additive correction to the measured potentials (see Section 7), after which the procedure is exactly as if  $H$  and  $G$  were strictly constant during a titration.

The volume  $H$  c.c. is, as it were, a "natural" unit-quantity of the reagent solution, in terms of which  $X$  represents distance from the equivalence point. Since  $U$  vanishes with  $X$  (i.e., at the equivalence point),

$$E_e = \bar{E}_0 - RTG_e/F \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$U = F(E - E_c)/RT + (G - G_c) \quad . \quad . \quad . \quad (25)$$

where  $E_e$  and  $G_e$  are the equivalence-point values of  $E$  and  $G$ . But the difference  $(G - G_e)$  is either negligible or is made so by the application of the corrections just mentioned, so that essentially  $U$  represents distance from the equivalence point in terms of the unit  $RT/F$  ( $= 25.00$  millivolts at  $17.0^\circ$ ).

### Section 3. Characteristic Forms of the Titration Curve.

*The Electrode-valencies.*—Some examples of the curves represented by the general equation (2), are exhibited in Fig. 1. The intersection of the axes represents the point of exact equivalence, and the positive direction of  $X$  is towards the left, so that the progressive addition of the reagent is represented by moving from left to right, as is customary in titration diagrams.

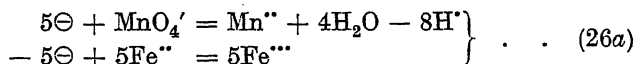
The forms of the curves will be better appreciated when considered in conjunction with the corresponding curves (Fig. 2), in which  $dU/dX$  is plotted against  $X$ . It is noticeable that the maxima in Fig. 2, and correspondingly the points of inflexion in Fig. 1, do not occur at the equivalence point except in the symmetrical cases where  $\alpha = \beta$ . Actually (see Section 4) they occur where  $(\alpha + \beta)U = 2 \log (\beta/\alpha)$ . Any one of the curves in Fig. 1, when rotated about the origin through  $180^\circ$ , coincides with the curve obtained by interchanging  $\alpha$  and  $\beta$ .

The parameters  $\alpha$  and  $\beta$ , which characterise the curves, are by definition equal to the ratios  $v/a$  and  $v/b$  respectively, and from (13) and (14) it is seen that 1 g.-mol. of the titrated substance "reacts" with  $v/a$  faradays of electricity in one of the electrode reactions, while in the other, 1 g.-mol. of the reagent reacts with  $v/b$  faradays.

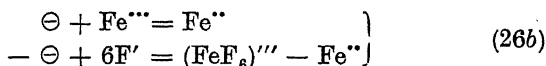
For instance, in a precipitation reaction, with an indicator electrode behaving as a "soluble" electrode towards either of the precipitated ions,  $\alpha$  and  $\beta$  would be the valencies of the two ions.

More generally, therefore, the term "electrode-valency" may be used to signify the number of faradays of electricity reacting with 1 g.-mol. of a given substance in a particular electrode-reaction. Thus  $\alpha$  and  $\beta$  are the electrode-valencies of A and B in this system.

In many cases, though not all, the electrode-valency is simply the ratio of the molecular weight to the equivalent weight ordinarily used in volumetric analysis. For instance, it is 5 for the permanganate ion and 1 for the ferrous ion, with a platinum electrode, the electrode reactions being



Similarly, in the iodate titration (p. 1429), equations (7) and (8) show that the electrode-valencies of the two principal reactants, iodate ion and sulphur dioxide, are respectively 5 and 2. On the other hand in Greeff's titration of fluoride ion by ferric ion, as applied potentiometrically by Treadwell and Köhl (*Helv. Chim. Acta*, 1925, 8, 500), the electrode-valency would not be equal to the ratio of the molecular weight to the ordinarily accepted equivalent weight, for here the alternative electrode reactions are



whence the electrode-valencies of ferric and fluoride ions would be 1 and  $\frac{1}{6}$ , respectively.

#### Section 4. Some Mathematical Properties of the Curves.

The curves in Fig. 1 are graphs of the function  $\sinh U$  for various assigned values of the parameters  $\alpha$  and  $\beta$ . If the positive directions of both axes of co-ordinates are reversed, the curves then represent the complementary function  $\sinh U$ , for

$$-\sinh(-U) = \frac{1}{2}(e^{\beta U} - e^{-\alpha U}) = \sinh U \quad (27)$$

Correspondingly, there are two complementary cosine functions,

$$\cosh U = \cosh(-U) = \frac{1}{2}(e^{\alpha U} + e^{-\beta U}) \quad (28)$$

and the other functions are obtained from these according to the usual conventions, e.g.,  $\tanh U = \sinh U / \cosh U$ , and  $\text{sech } U = 1 / \cosh U$ .

If, now, the purely numerical constants,  $(\alpha\beta\beta\alpha)^{1/(\alpha+\beta)}$  and  $\frac{1}{\alpha+\beta} \log\left(\frac{\alpha}{\beta}\right)$ , are represented by  $h$  and  $g$  respectively, the first

derivative of  $\frac{dU}{dX}$   $U$  (or  $dX/dU$ ) can be written in the form  $\frac{1}{\cosh(U+g)}$ , and it is the reciprocal of this, i.e.,  $dU/dX$  or  $\frac{1}{\cosh(U+g)}$ , which is plotted against  $X$  in Fig. 2. Similarly, the first derivative of  $\cosh U$  is  $\sinh(U+g)$ , and it follows that the second derivative of  $\sinh U$  is  $\cosh(U+2g)$ . Thus each curve in Fig. 1 has a point of inflexion where  $U = -2g$  and  $X = -\sinh 2g$ . This is the point of maximal slope and sensitivity (see Section 9), the maximal value of  $dU/dX$  being  $\cosh g$ . The following table shows the values of these characteristic constants for several types of curve. In the last column the quantity  $50g$  is tabulated, being the distance of the point of inflexion from the equivalence point in millivolts at  $17^\circ$  (i.e.,  $RT/F \cdot 2g$ ).

$\alpha.$	$\beta.$	$h.$	$g.$	$-X_{\text{infl.}}$	$\left(\frac{dX}{dU}\right)_{\text{min.}}$	$\left(\frac{dU}{dX}\right)_{\text{max.}}$	$E_e - E_{\text{infl.}}$
1	1	1	0	0	1	1	0
2	1	1.26	0.231	0.59 <sub>6</sub>	1.19 <sub>2</sub>	0.83 <sub>8</sub>	11.5 <sub>5</sub>
3	1	1.31 <sub>4</sub>	0.274 <sub>7</sub>	0.77	1.15 <sub>5</sub>	0.86 <sub>5</sub>	13.7 <sub>3</sub>
5	1	1.30 <sub>8</sub>	0.268 <sub>2</sub>	0.82 <sub>2</sub>	1.02 <sub>5</sub>	0.97 <sub>5</sub>	13.4
6	1	1.29 <sub>2</sub>	0.256	0.81 <sub>2</sub>	0.97 <sub>5</sub>	1.02 <sub>5</sub>	12.8
2	2	2	0	0	2	0.5	0
3	2	2.35 <sub>2</sub>	0.081 <sub>1</sub>	0.38 <sub>4</sub>	2.30 <sub>1</sub>	0.434	4.0 <sub>3</sub>
5	2	2.59 <sub>8</sub>	0.131	0.70 <sub>9</sub>	2.36	0.424	6.5 <sub>5</sub>
1	$\frac{1}{2}$	0.215 <sub>3</sub>	1.535 <sub>8</sub>	0.81 <sub>2</sub>	0.162 <sub>5</sub>	6.16	76.7 <sub>9</sub>

Interchange of the values of  $\alpha$  and  $\beta$  in any case alters the sign of  $X_{\text{ind}}$ ,  $g$ , and of  $E_e - E_{\text{ind}}$ , but makes no other difference. It is noticeable that  $\left(\frac{dX}{dU}\right)_{\min.}$ , or  $h \cosh g$ , always approximates  $\beta_\alpha$  in value to the smaller of the two electrode-valencies.

### Section 5. General Application of Method I.

Equation (2) has two limiting forms,

$$X = \frac{1}{2} e^{aU} \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

$$-X = \frac{1}{\beta} e^{-\beta U} \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

valid respectively for large positive and large negative values of  $U$ . One or other of these will be accurate to 1% as regards  $X$ , unless  $U$  lies between the limits  $\pm (\log 100)/(\alpha + \beta)$ ; and the region defined by these limits, some  $230/(\alpha + \beta)$  millivolts in extent, within which the incompleteness of the analytical reaction exceeds 1%, may be referred to as the "equivalence region." Outside this region Method I is applicable and the result of the titration

can be determined from a single change of the potential  $E$ , without knowledge of  $E_e$ ,  $\bar{E}_0$ ,  $G$ , or  $H$ , as follows.

Fully written, equation (29) is equivalent to

$$E = E_0 + \frac{RT}{\alpha F} \log \frac{nM}{V} \gamma_A \theta_A - \frac{RT}{\alpha F} \Sigma \frac{p}{a} \log C_F \gamma_F. \quad (31)$$

which is therefore valid at all points or stages outside and *before* the equivalence region. Consider two such points,  $(E, M)$  and  $(E', M')$ , separated by  $\epsilon$  millivolts and  $m$  c.c. of reagent solution (compare Part I, Section 4). Suppose that at the earlier stage,  $(E', M')$ , the amount of the (typical) subsidiary substance P in the titrated solution is  $nM_P$  mg.-equivs. [all equivalents being reckoned according to the chemical equation (12)], then if the volume of the solution is  $V'$  c.c.,

$$E' = E_0 + \frac{RT}{\alpha F} \log \frac{nM'}{V'} \gamma_A \theta_A - \frac{RT}{\alpha F} \Sigma \frac{p}{a} \log \frac{nM_P}{V'} \gamma_F. \quad (32)$$

Now, on the addition of  $m$  c.c. of the reagent solution, not only is the amount of the titrated substance diminished to  $nM$  mg.-equivs., but the volume of the solution is increased to  $V$  c.c., and also the amount of the subsidiary substance, P, is either increased or decreased by  $mn$  mg.-equivs., according as this substance is, on the whole, a product or a reactant in the analytical reaction (*i.e.*, not merely according as  $p$  is positive or negative).

At the later stage, therefore, assuming for the present (see Part I, Sections 2 and 7) that change in the adsorption and activity coefficients can be neglected,

$$E = E_0 + \frac{RT}{\alpha F} \log \frac{nM}{V} \gamma_A \theta_A - \frac{RT}{\alpha F} \Sigma \frac{p}{a} \log n \frac{M_P \pm m}{V} \gamma_F. \quad (33)$$

where  $E = (E' - \epsilon)$ ,  $M = (M' - m)$ , and  $V = (V' + m)$ . Then, by subtraction,

$$\epsilon = \epsilon_m + \epsilon_v \left( 1 - \Sigma \frac{p}{a} \right) + \Sigma \frac{p}{a} \epsilon_P \quad (34)$$

where

$$\alpha \epsilon_m = RT/F \cdot \log (1 + m/M) \quad (35)$$

$$\alpha \epsilon_v = RT/F \cdot \log (1 + m/V') = -RT/F \cdot \log (1 - m/V) \quad (36)$$

$$\alpha \epsilon_P = RT/F \cdot \log (1 \pm m/M_P) \quad (37)$$

The effect of the change in the amount of A is represented by  $\epsilon_m$ , while the effects of the simultaneous changes in the "subsidiary conditions" (the volume of the solution and the amounts of the



subsidiary substances) are represented by the remaining terms on the right of equation (34). In this sense  $\epsilon_m$  is the value of the measured potential change "corrected to constant subsidiary conditions," and the correction terms,  $\epsilon_v$ ,  $\epsilon_P$ , etc., are to be found from the tables provided in Part I (*loc. cit.*). It is obvious that, as indicated in Part I, changes in the adsorption and activity coefficients (if not negligible, as assumed) could be corrected for in an entirely similar manner. The result of the titration then follows from the relation

$$M = m \cdot f(\alpha\epsilon_m) \quad (38)$$

[see Part I, Table I and equations (22) and (26)].

In Part I, the use of the dilution term  $\epsilon_v$  is fully demonstrated, a convenient procedure being indicated in Section 12, and a type of case being discussed in Section 8, in which this correction is eliminated owing to the fact that  $\Sigma p/a$  is equal to unity. The latter section includes an example of a correction of the  $\epsilon_P$  type, P being a product of the reaction (ferrie or titanic ion). In this case, on the assumption that P is absent at the commencement of the titration,  $M_P$  is accurately known, being simply the number of c.c. of reagent solution already added before the further addition of the  $m$  c.c.

On the other hand, in many cases P will be a substance present in considerable excess,  $M_P$  will be large in comparison with  $m$ , and therefore only a rough estimate (if any) of its magnitude will be required in order to determine the very small correction,  $\epsilon_P$ . An example of this would be hydrogen ion as a subsidiary substance in most oxidation-reduction titrations. In short, it is plain that in any particular case, under suitable conditions, the correction of the measured potential changes will readily be reduced to a simple routine.

One special advantage of Method I is that it makes use of less than one half or side of the titration curve, being independent of the equivalence region as well as of all that part of the curve beyond it. This is notably useful in the titration of mixed solutions (*e.g.*, a mixture of halides), where the curves corresponding to the successive reactions overlap and truncate one another. Nevertheless, if the second half of the curve happens to be available, it may be utilised in essentially the same way, the full form of equation (30), valid here, being

$$-E = -E'_0 + \frac{RT}{\beta F} \log \frac{nM}{V} \gamma_B \theta_B - \frac{RT}{\beta F} \Sigma \frac{q}{b} \log C_c \gamma_c \quad (39)$$

If ( $E$ ,  $M$ ) and ( $E''$ ,  $M''$ ) are the two successive stages, both beyond the equivalence region, and separated by  $\epsilon'$  millivolts and  $m'$  c.c.

of reagent solution, so that  $E'' = (E - \varepsilon')$ ,  $M'' = (M - m')$ , and  $M$  is negative, we find

$$\varepsilon' = \varepsilon'_m - \varepsilon'_v (1 - \Sigma q/b) \quad . \quad . \quad . \quad (40)$$

where  $\beta \varepsilon'_v = RT/F \cdot \log (1 + m'/V) \quad . \quad . \quad . \quad (41)$

$$\beta \varepsilon'_m = RT/F \cdot \log \left( 1 + \frac{m'}{-M} \right) \quad . \quad . \quad . \quad (42)$$

and therefore  $-M = m' \cdot f(\beta \varepsilon'_m) \quad . \quad . \quad . \quad (43)$

No correction term of the  $\varepsilon_p$  (or  $\varepsilon_q$ ) type occurs here, because the chemical reaction has ceased and the *quantities* of the subsidiary substances are not changing.

It has been assumed, so far, that B is the only significant substance (apart from the solvent) introduced by means of the reagent solution. If, however, the latter contains also appreciable quantities of any of the subsidiary substances, or of compounds capable of reacting with the latter (for examples, see Section II), this merely involves obvious modifications in the form of the subsidiary-conditions correction, for it remains true, in general, that the changes in these conditions are proportional to the quantities of reagent solution added.

In using Method I, should the stage ( $E$ ,  $M$ ) be allowed to fall within the equivalence region, the result of the titration will be too high if obtained from the first half of the curve, and too low if from the second half. If  $M_{app.}$  is the erroneous value of  $M$  so found, the error in the former case is approximately  $(H/2)^{1+\beta/\alpha} / M_{app.}^{\beta/\alpha}$ , and the same with  $\alpha$  and  $\beta$  interchanged in the latter case. In either case, an alternative formulation of the error is  $M_{app.} \cdot f[(\alpha + \beta)(E \sim E_e)]$ .

Thus, approximate knowledge of *either*  $H$  or  $E_e$  would permit the correction of this error if not too large. Such procedure, of course, would really constitute a crude form of Method II.

### Section 6. General Forms of Methods II and III.

Apart from its special advantages, the absolute precision of Method I is higher than that attainable under the most favourable conditions by the customary potentiometric methods. Sometimes, however (as when dealing with unusually dilute solutions or with an analytical reaction of low inherent sensitivity), it may be desirable to seek the appreciable increase of precision which is, in general, to be obtained by making use of a stage nearer to the point of inflexion than is permissible in Method I. Of the two distinct methods of so doing, Method II makes use of only one half or side of the titration curve, but requires some knowledge of the unit  $H$ , whereas Method III requires no knowledge of  $H$  but utilises both halves of the curve. Properly applied, either method yields the highest absolute precision

obtainable with a given experimental system. Potentiometric methods of the "absolute" type (see introductory remarks in Part I) should theoretically yield the same maximal precision, but in practice this is not realised because the absolute values of the measured potential are not nearly so accurately reproducible as are the differences or changes on which alone the differential methods depend.

*Method II.*—Consider, as in the last section, two successive stages ( $E'$ ,  $M'$ ) and ( $E$ ,  $M$ ), separated by  $\epsilon$  millivolts and  $m$  c.c. of reagent solution; but suppose, now, that the second stage lies within the equivalence region, so that the limiting form (31) is not valid at this stage. Applying, instead, the general equation, we may write

$$M/H = \sinh_{\alpha\beta} U \quad . \quad . \quad . \quad (44)$$

where  $U$  is defined by equation (23).

At the earlier stage the measured potential has the value  $E'$ , or ( $E + \epsilon$ ), but this is, in effect, "corrected" to a value ( $E + \epsilon_m$ ), in the manner to be explained in the following section, whereupon both  $H$  and  $G$  may be treated as constants; hence, using the same value of  $H$  as in (44),

$$(M + m)/H = \sinh_{\alpha\beta} (U + u) \quad . \quad . \quad . \quad (45)$$

where

$$u = F/RT \cdot \epsilon_m \quad . \quad . \quad . \quad (46)$$

Now the following identity can easily be verified,

$$\sinh_{\alpha\beta} (U + u) - \sinh_{\alpha\beta} U = \sinh_{\alpha\beta} u \cdot \cosh_{\alpha\beta} (U + \phi) \cdot \operatorname{sech}_{\alpha\beta} \phi \quad (47)$$

where  $(\alpha + \beta)\phi = \log \frac{1 + f(\beta\epsilon_m)}{f(\alpha\epsilon_m)} \quad . \quad . \quad . \quad (48)$

or, for large values of  $\epsilon_m$ ,

$$(\alpha + \beta)\phi \approx \alpha u + f(\beta\epsilon_m) - f(\alpha\epsilon_m) \quad . \quad . \quad (49)$$

$$\approx \alpha u \quad . \quad . \quad . \quad (50)$$

Thus, if equation (48) is written in the form

$$\operatorname{sech}_{\alpha\beta} (U + \phi) = (H/m) \sinh_{\alpha\beta} u \cdot \operatorname{sech}_{\alpha\beta} \phi \quad . \quad (51)$$

and coupled with equation (44), it is apparent that when  $m$  and  $\epsilon$  have been measured and  $H$  is known,  $M$  may be obtained by the use of a parallel table of the functions  $\sinh_{\alpha\beta}$  and  $\operatorname{sech}_{\alpha\beta}$  in a manner essentially similar to that described in Part II (pp. 862, 863). The corresponding curves shown in Figs. 1 and 2 would be a (less accurate) substitute for such tables since there is no objection to dividing both sides of equation (51) by  $h$ . Alternatively, of course, suitable

diagrams, after the manner of those shown in Part II (Figs. 1 and 2), could be constructed.

*Method III.*—Introducing a third and later stage ( $E''$ ,  $M''$ ) beyond the equivalence region and separated from the second stage by  $\epsilon'$  millivolts and  $m'$  c.c. of reagent solution, and supposing as before that the correction of Section 7 is applied, the measured potential ( $E - \epsilon'$ ) being corrected to ( $E - \epsilon'_m$ ), then we have

$$(M - m')/H = \sinh \frac{(U - u')}{\alpha\beta} \quad . \quad . \quad . \quad (52)$$

where

$$u' = F/RT \cdot \epsilon'_m \quad . \quad . \quad . \quad (53)$$

Between the three equations (44), (46), and (53), both  $H$  and  $U$  can be eliminated, and the following exact equation obtained,

$$M = \frac{m \operatorname{cosech} \frac{u}{\alpha\beta} - m' \operatorname{cosech} \frac{u'}{\beta\alpha}}{\coth \frac{u}{\alpha\beta} + \coth \frac{u'}{\alpha\beta} - \operatorname{cosech} \frac{u}{\alpha\beta} - \operatorname{cosech} \frac{u'}{\beta\alpha}} \quad . \quad (54)$$

For large values of  $u$  and  $u'$ , such as will in practice be used, equation (54) can be reduced to the much more convenient approximate form

$$M_{app} = m \cdot f(\alpha\epsilon_m) - m' \cdot f(\beta\epsilon'_m) \quad . \quad . \quad . \quad (55)$$

The error involved in this approximation is of the order of magnitude of

$$(m - m' + 2M_{app}) \cdot f(\alpha\epsilon_m + \beta\epsilon'_m) \quad . \quad . \quad . \quad (56)$$

and so is negligible when  $\epsilon_m$  and  $\epsilon'_m$  are both large.

Equations (29) and (30) of Part II are complicated by the terms involving  $V$  which there represent (approximate) allowance for volume change, but on omitting these terms and (in compensation) altering  $\epsilon$  and  $\epsilon'$  to  $\epsilon_m$  and  $\epsilon'_m$ , we see that these equations represent the special case where  $\alpha = \beta = 1$  (see examples in Section 7).

### Section 7. Correction for Variation in $H$ and $G$ .

It is essential to the increased precision of Methods II and III, as compared with Method I, that the stage ( $E$ ,  $M$ ) should lie within the equivalence region, so that equation (33), for example, no longer holds good. Nevertheless, the additive corrections (described in Section 5) for change in the subsidiary conditions are still essentially valid, being equivalent in effect to making  $H$  and  $G$  constant, with the values they attain at the stage ( $E$ ,  $M$ ). For, consider again the stage ( $E'$ ,  $M'$ ) which is outside and before the equivalence region, so that equation (32) still applies. If, now, without altering the amount ( $nM$  mg.-equivs.) of the titrated substance, we could alter the subsidiary conditions, the volume from  $V'$  to  $V$ , and the amount

of the subsidiary substance P from  $nM_P$  to  $n(M_P \pm m)$  mg.-equivs., etc., it is obvious that  $E'$  would be altered to

$$E'(\text{corr.}) = E' - \varepsilon_v \left(1 - \frac{\Sigma p}{a}\right) - \frac{\Sigma p}{a} \varepsilon_P \quad . \quad . \quad (57)$$

where  $\varepsilon_v$  and  $\varepsilon_P$  are defined by equations (36) and (37). Now, at the stage ( $E, M$ ) the subsidiary conditions *actually* are  $V$ , and, to a close approximation,  $n(M_P \pm m)$ , etc., the error of the latter approximation (due to the incompleteness of the analytical reaction) being only  $\frac{1}{2}nH\epsilon^{\beta U}$ , which may be neglected in comparison with  $nM_P$ . In other words,  $E'(\text{corr.})$  is the value the potential would possess at the stage ( $E', M'$ ) *if the subsidiary conditions (and therefore H and G) had those values which they actually attain at the stage ( $E, M$ )*.

Since  $E' = (E + \varepsilon)$ , we may write

$$E'(\text{corr.}) = (E + \varepsilon_m) \quad . \quad . \quad . \quad (58)$$

where  $\varepsilon_m$  is defined by equation (34). In an exactly similar manner, it can be shown that if  $\varepsilon'_m$  is defined by equations (40) and (41), the value which the potential would possess at the stage ( $E'', M''$ ) (which is *beyond* the equivalence region), if  $H$  and  $G$  still had those values which they actually attained at the stage ( $E, M$ ), is

$$E''(\text{corr.}) = (E - \varepsilon'_m) \quad . \quad . \quad . \quad (59)$$

In applying these corrections, it is usually convenient to adopt the procedure indicated in Part I, Section 12, correcting the measured potentials to some simple round value of each subsidiary condition. It is true that such correction is artificial as applied to the stage ( $E, M$ ) because the latter is in the equivalence region, and the corrected value of  $E$  will not be the value it would attain if the subsidiary conditions were altered to the stated round values. Nevertheless, if  $E$  is corrected in the same manner as  $E'$ , the difference between these corrected values will be  $\varepsilon_m$ , as defined above. And similarly, if  $E$  is corrected in the same manner as  $E''$ , *i.e.*, as if it were *beyond* the equivalence region, then the difference between the corrected  $E$  and  $E''$  will be  $\varepsilon'_m$  as defined above.

For example, take the simple case of the chloride titrations recorded in Part II (p. 868). As explained there, the *E.M.F.* of the silver chloride-quinhydrone cell used is doubly affected by dilution when the chloride is in marked excess, and is unaffected by dilution when the silver ion is in excess. In this case, therefore, equations (34) and (40) assume the special forms

$$\begin{aligned}\varepsilon_m &= \varepsilon - (2RT/F) \cdot \log V/V' \\ \varepsilon'_m &= \varepsilon'\end{aligned}$$

Now if  $E'$  is corrected to some convenient volume, such as 100 c.c., it becomes (say)  $E'_a$  by addition of a correction of the first form,

$$\text{Corr. (a)} = (2RT/F) \cdot \log V'/100 \quad (60)$$

$$E'_a = E' + (2RT/F) \cdot \log V'/100 \quad (61)$$

and if  $E$  is "corrected" in the same manner,

$$E_a = E + (2RT/F) \cdot \log V/100$$

then, by subtraction,

$$E'_a - E_a = \varepsilon - (2RT/F) \cdot \log V/V' = \varepsilon_m.$$

On the other hand,  $E''$  is corrected to any convenient volume by the addition of a different form of correction, which in this particular case is zero,

$$\text{Corr. (b)} = 0 \quad (62)$$

$$E''_b = E'' \quad (63)$$

and, of course, on "correcting"  $E$  in the same way and subtracting,

$$E_b - E''_b = \varepsilon' = \varepsilon'_m.$$

For the sake of comparison, two of the titrations recorded in Part II (Examples 1 and 2, p. 868) are worked out below according to the newer and generally applicable procedure, which will be seen to be also much simpler arithmetically. In order to make the examples more generally illustrative, the second form of correction [Corr. (b)] is explicitly stated and applied, although in this special case it happens to be zero throughout.

*Example 1.* 1000 C.c. of  $N/1000\text{-KCl}$  titrated by  $N/100\text{-AgNO}_3$  (actually known to be equivalent to 98.5 c.c. of  $\text{AgNO}_3$ , but titrated as if only known to be stronger than  $N/2000$ ); temp.  $\approx 14.5^\circ$ .

The application of Method III begins at Stage II, when 85 c.c. of silver nitrate have already been added in applying Method I. The latter method having shown that between 13 and 14 c.c. are still required to reach equivalence, two successive additions of 13 c.c. and 12 c.c. respectively are made, and the potentials at Stages III and IV measured. The three measured potentials are corrected to  $17^\circ$ , and then the first and second are corrected to 1000 c.c. volume in the manner (a) [see equations (60) and (61)], and the second and third to any convenient volume in the manner (b) [see equations (62) and (63)], and  $\varepsilon_m$  and  $\varepsilon'_m$  are obtained by subtraction.

Stage.	$V$ 1000	Corr. (a).	Corr. (b).	$E$ (expt.).	$E_{17^\circ}$ .	$E_a$ .	$E_b$ .
II	1.085	4.0 <sub>5</sub>		172.2	173.6 <sub>5</sub>	177.7	
III	1.098	4.6 <sub>5</sub>	0	118.1	119.1	123.7 <sub>5</sub>	119.1
IV			0	58.3	58.8		58.8
				By subtraction		53.9 <sub>5</sub>	60.3

Then, to find  $M$  at Stage III, and hence  $M_0$  :

$$\begin{array}{llll} m = 13 & \epsilon_m = 53.9_5 & f(\epsilon_m) = 0.130_2 & m \cdot f(\epsilon_m) = 1.69_3 \\ m' = 12 & \epsilon'_m = 60.3 & f(\epsilon'_m) = 0.098_8 & m' \cdot f(\epsilon'_m) = 1.18_3 \end{array}$$

By subtraction,  $M = 0.51$   
and by addition of 98.0,  $M_0 = 98.51$

*Example 2.* 100 C.c. of  $N/1000\text{-KCl}$  titrated by  $N/1000\text{-AgNO}_3$  (actually known to be equivalent to 98.5 c.c. of  $\text{AgNO}_3$ , but titrated as if only known to be stronger than  $N/4000$ ); temp.  $\sim 20^\circ$ .

The procedure is essentially as in Example 1, except that two stages (III and IV) within the equivalence region are used, in turn, as the stage ( $E$ ,  $M$ ), so that two results are obtained which are then averaged.

For the purpose of the dilution correction, 100 c.c. is taken as a convenient round value of the volume.

Stage.	$\frac{V}{100}$	Corr. (a).	Corr. (b).	$E$ (expt.).	$E_{17.5}$	$E_a$	$E_b$
II	1.75	28.0		190.4	188.5	216.5	
III	1.96	33.6 <sub>5</sub>	0	139.8	138.4	172.0 <sub>5</sub>	138.4
IV	2.00	34.6 <sub>5</sub>	0	120.5	119.3	153.9 <sub>5</sub>	119.3
V			0	68.4	67.7		67.7
By subtraction							
						$\begin{cases} 44.4_5 \\ 62.5_5 \end{cases}$	$\begin{cases} 70.7 \\ 51.6 \end{cases}$

(i) To find  $M$  at Stage III, and hence  $M_0$  :

$$\begin{array}{llll} m = 21 & \epsilon_m = 44.4_5 & f(\epsilon_m) = 0.2034 & m \cdot f(\epsilon_m) = 4.27_1 \\ m' = 29 & \epsilon'_m = 70.7 & f(\epsilon'_m) = 0.0629 & m' \cdot f(\epsilon'_m) = 1.82_4 \end{array}$$

By subtraction,  $M = 2.45$   
By adding 96.0,  $M_0 = 98.45$

(ii) To find  $M$  at Stage IV, and hence  $M_0$  :

$$\begin{array}{llll} m = 25 & \epsilon_m = 62.5_5 & f(\epsilon_m) = 0.0892_8 & m \cdot f(\epsilon_m) = 2.23_1 \\ m' = 25 & \epsilon'_m = 51.6 & f(\epsilon'_m) = 0.1454 & m' \cdot f(\epsilon'_m) = 3.63_5 \end{array}$$

By subtraction,  $M = -1.40$   
By adding 100.0,  $M_0 = 98.60$   
Average of two results in Example 2,  $M_0 = 98.52_5$ .

In Example 2, the values of Corr. (a) are seen to be large, but this does not mean that it will be liable to introduce appreciable errors into the result of the titration, or that the subsidiary condition  $V$  needs to be very accurately known, for it is only the *change* in Corr. (a)—amounting to 6.65 millivolts in all—which affects the corrected difference  $\epsilon_m$ .

### Section 8. Complete Temperature Correction.

If, as in the above examples, the measured potentials are multiplied by  $(290/T)$ , this has the effect of multiplying the differences  $\epsilon$  and  $\epsilon'$  by the same factor, which makes allowance for the fact that the unit  $(RT/F)$  is proportional to the absolute temperature.

This is all that is required so long as the temperature does not vary much during a titration.

In working at temperatures other than "room temperature," however, considerable fluctuations are not easily avoided under practical conditions for titration. Even if a thermostat is used it is very troublesome to keep the reagent at the same temperature, while, if it is not so kept, time is lost after each addition in waiting for temperature equilibrium. It is therefore quicker and simpler to make no attempt to maintain a fixed temperature, but to read the thermometer at each stage and apply a complete temperature correction in the following manner.

For such variation as will occur during a titration both  $E_0$  and  $E'_0$  may be assumed to depend linearly on the temperature. This means that if the temperature coefficient of the potential  $E$  is measured at *any* stage outside the equivalence region, the quantity  $(E - T \cdot dE/dT)$  will be found to possess one or other of two values, say  $E_{00}$  and  $E'_{00}$ —the former at any stage *before* the equivalence region, the latter at any *beyond* it. Two such measurements will therefore suffice to determine these two constants, which are all that we require for the purpose of the complete temperature correction.

If  $T'$ ,  $T$ , and  $T''$  are the temperatures of the system at the successive stages  $(E', M')$ ,  $(E, M)$ , and  $(E'', M'')$  in Method III, it is easily shown that when the potential changes,  $\epsilon$  and  $\epsilon'$ , are corrected for the *variation* of temperature during titration, as well as for the value of the unit,  $RT/F$ , they become

$$\epsilon_{17} = 290(E' - E_{00})/T' - 290(E - E_{00})/T \quad . \quad (64)$$

$$\epsilon'_{17} = 290(E - E'_{00})/T - 290(E'' - E'_{00})/T'' \quad . \quad (65)$$

so that for differential purposes  $290(E' - E_{00})/T'$  and  $290(E'' - E'_{00})/T''$  may be used as temperature-corrected values of  $E'$  and  $E''$  respectively, while  $E$  has two such values—one  $290(E - E_{00})/T$ , as if it were *before* the equivalence region, and the other  $290(E - E'_{00})/T$ , as if it were *beyond* that region. There is here an obvious analogy in principle with the procedure discussed in the latter part of Section 7. If  $\epsilon_{17}$  is re-written in the form

$$\epsilon_{17} = \frac{290}{T} \left[ \left\{ \frac{T}{T'} (E' - E_{00}) + E_{00} \right\} - E \right] \quad . \quad (66)$$

its derivation will be obvious, and it will be seen that the accuracy of the correction depends on the assumption that  $(E' - E_{00})$  is proportional to the absolute temperature over some range including  $T$  and  $T'$  *but not necessarily including*  $290^\circ$  Abs. That it does not



depend on accurate knowledge of  $E_{00}$  will be seen if  $\varepsilon_{17}$  is again re-written as

$$\varepsilon_{17} = \frac{290}{T'} E' - \frac{290}{T} E + \left( \frac{290}{T} - \frac{290}{T'} \right) E_{00} \quad (67)$$

since the coefficient of  $E_{00}$  is small. Similar considerations apply to  $\varepsilon'_{17}$ .

### Section 9. Precision of the Generalised Method.

Writing  $U'$  for  $(U + u)$ , and using the abbreviations  $\Delta \operatorname{sech}$  and  $\Delta \tanh$  for the positive differences  $[\operatorname{sech}_{\alpha\beta}(U + g) - \operatorname{sech}_{\alpha\beta}(U' + g)]$  and  $[\tanh_{\alpha\beta}(U' + g) - \tanh_{\alpha\beta}(U + g)]$  respectively, we may formulate the error  $dM$  of a titration by Method II as follows :

$$-dM = \frac{Hh}{\Delta \operatorname{sech}} du + \frac{\Delta \tanh}{\Delta \operatorname{sech}} (\cosh g)_{\beta\alpha} dH \quad (68)$$

where  $du$  and  $dH$  represent (small) errors in  $u$  and  $H$ . Under the conditions of highest sensitivity, when  $U \approx -2g$  and  $u$  is large, this reduces to

$$-\frac{dM}{h \cdot \cosh g}_{\beta\alpha} \approx H \cdot du + \frac{dH}{\beta} \quad (69)$$

and it has been seen (Section 4) that  $h \cdot \cosh g$  is approximately equal to the smaller of the two electrode-valencies.

Similarly, writing  $U''$  for  $(U - u')$ , and  $\Delta' \operatorname{sech}$  and  $\Delta' \tanh$  for the analogous positive differences, due regard being paid to the fact that  $u$  and  $u'$  have opposite signs, we derive the following equation for the error of a titration by Method III :

$$\frac{dM}{Hh} \left[ \frac{\Delta \operatorname{sech}}{\Delta \tanh} + \frac{\Delta' \operatorname{sech}}{\Delta' \tanh} \right] = \frac{du'}{\Delta' \tanh} - \frac{du}{\Delta \tanh} \quad (70)$$

which is the generalised form of equation (37) of Part II.

Under optimum conditions, when  $U \approx -2g$  and both  $u$  and  $u'$  are large, equation (70) reduces to

$$\frac{dM}{Hh \cosh g} \approx \frac{\alpha du' - \beta du}{\alpha + \beta} \quad (71)$$

showing that (under these conditions) equal and opposite errors in  $u$  and  $u'$  will have the same effect as a single error of the same magnitude as either in  $u$  in Method II. The precision of Method II, however, depends also on the correctness of the value assigned to  $H$ . Thus from equation (69),  $-\partial M / \partial H$  would be approximately equal to either unity or  $\alpha/\beta$  according as  $\alpha$  is greater or less than  $\beta$ , i.e., it would not be greater than unity and might be much less.

Of course, Method II, like Method I, can be applied to the second half of the curve if this is available. For this case equation (68) would be modified in an obvious manner, and instead of equation (69) we should have

$$\frac{dM}{h \cosh g_{\beta a}} \approx H \cdot du' + \frac{dH}{\alpha} \quad (72)$$

showing that the maximal sensitivity is the same, but  $\partial M / \partial H$  is now (approximately) equal to either unity or  $\beta / \alpha$ .

### Section 10. An Alternative Geometrical Form of Method I.

*The Straight-line Method.*—If, as in Section 7,  $E_a$  represents the value of the measured potential when “corrected” in the manner proper to any stage before the equivalence region, then equation (31) is equivalent to  $E_a = \text{constant} + RT / \alpha F \cdot \log M$ . The (unknown) constant may be written in the form  $-RT / \alpha F \cdot \log k$ , and  $E_a$  in the substituted form  $RT / \alpha F \cdot \log y$ , whereupon the equation reduces to  $ky = M = M_0 - (M_0 - M)$ , where  $y$  is equal to  $e^{(\alpha F / RT) E_a}$ .

If, then, the corrected potential at each stage is plotted on a suitable *exponential scale*, against the number of c.c. of reagent present, the successive points *will lie on a straight line*, which cuts the axis at a point indicating the result of the titration. Thus two points or stages suffice to determine the result (the more accurately if they are well separated), but also, owing to the exponential scale, it will be found that the determination becomes very much more certain as the final measurement more nearly approaches the equivalence point, provided always that it do not fall within the equivalence region. All this corresponds exactly with the conditions of precision in the ordinary or algebraic form of the method.

The geometrical form, however, provides a useful general method for investigating new or uncertain systems, since if a number of points are plotted (instead of merely two) their adherence to a straight line is a strong indication, amounting almost to conclusive proof, that equilibrium conditions are being realised.

A suitably graduated scale is easily constructed. The distances being proportional to  $e^x$ , the graduations are placed at convenient intervals of  $(RT / \alpha F)x$  [or, for  $17^\circ$ ,  $(25 / \alpha)x$ ] and numbered consecutively in millivolts, *commencing with any convenient number*. The test and the certainty of the result can be improved if the second half of the titration curve is available, for, corresponding to this, a second straight line should be obtainable, passing through the same end-point, the equation being  $k'y' = (M_0 - M) - M_0$ , where  $y' = e^{-(\beta F / RT) E_b}$ .

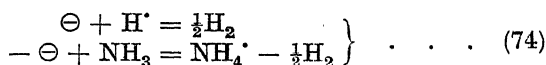
Section 11. *Importance of the Symmetrical Case.*

*Application in Acidimetry and Alkalimetry.*—It will be noticed that, even in the symmetrical case where  $\alpha = \beta$ , the titration-curve equation and the methods dependent on it are now much more general in application than those obtained in Part II, since the latter took no account of subsidiary reactants and products. For example, with the new equation, and the general form of subsidiary-conditions correction described in Section 7, the following important cases can be dealt with in a simple manner.

*Case (1).* In the titration of a *weak base* (such as ammonia) against a strong acid, the former being the added substance, the equation for the analytical reaction is properly written

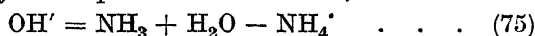


( $K$  being *ca.*  $5 \times 10^{-10}$ , *i.e.*,  $10^{-14}/2 \times 10^{-5}$  or  $K_w/K_b$ ) and if a hydrogen electrode or its equivalent is used as indicator electrode, the alternative electrode reactions are



The principal reactants are, in effect, hydrogen ion and the base, the amount of hydroxyl ion present being relatively quite negligible until far beyond the equivalence region, unless excessively dilute solutions are being used.

*Case (2).* Exactly the same equations are applicable to the titration of a *strong base* against a strong acid *in the presence of an appreciable amount of a salt of a weak base*, for in that case, owing to the weakness of the base, the addition of hydroxyl ions (*i.e.*, the strong base) is exactly the same in effect as adding an equivalent quantity of the *weak base* and, at the same time, withdrawing an equivalent quantity of the positive ion of its salt, thus

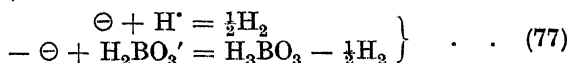


The additional molecule of water makes no difference, while the withdrawal of the positive ion only affects the form of the subsidiary-conditions correction.

*Case (3).* The titration of a *salt of a weak acid* against a strong acid is really entirely analogous to Case (1), the negative ion of the salt behaving essentially like the weak base. For example, with borax (which in solution is essentially  $\text{NaH}_2\text{BO}_3$  mixed with an equimolar quantity of free boric acid) the analytical reaction is

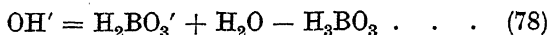


( $K$  being *ca.*  $10^{-9}$ ) and the electrode reactions are



The principal reactants are hydrogen ion and the dihydrogen-borate ion, and it is only an incidental matter affecting the form of the subsidiary-conditions correction that, in this particular case, an equivalent amount of free boric acid accompanies the added substance.

*Case 4.* From the same analogy, it follows that the equations of Case (3) are applicable to the titration of a strong base against a strong acid *in the presence of an appreciable amount of a weak acid*. The addition of the hydroxyl ion is exactly the same in effect as adding an equivalent quantity of the negative ion of the weak acid, and at the same time withdrawing an equivalent quantity of the weak acid itself :



and the latter withdrawal merely modifies the subsidiary-conditions correction.

Finally, four cases analogous to the above are obtained on interchanging the words "acid" and "base," making obvious equivalent alterations with regard to the ions, and adopting as indicator electrode either the hydrogen electrode or any other which behaves *in alkaline solution* as a "hydroxyl electrode." Treated in this manner, the eight cases are seen to be essentially one and the same, and the equations of this section, taken in conjunction with the preceding general theory, show how these common titrations of acidimetry and alkalimetry may be made to yield the highest possible precision.

#### *Summary.*

It is shown that both the titration-curve equation and the new methods of titration given in two previous papers can be fully generalised, *i.e.*, made applicable to a system involving both analytical and electrode reactions of the most general type.

The characteristic forms of the curves represented by the generalised equation, and of the derived curves, are indicated with the aid of diagrams, and some concrete examples cited. The more important mathematical properties of the curves are exhibited, the generalised methods of titration deduced, and their precision formulated, in terms of certain bin-exponential functions, regarded as generalised hyperbolic functions. Methods I and III, however, still involve only the single function, *f*, tabulated in the first of this series of papers.

A routine procedure previously indicated is now more fully developed, whereby, in connexion with all three methods, accurate allowance is made for unavoidable variations in the subsidiary conditions, *i.e.*, the volume of the solution and the concentrations

of subsidiary reactants and products. A simple mode of correction is also provided for any unavoidable *fluctuations* of temperature.

In Section 10, a *geometrical* form of Method I is outlined (a "straight-line method"), suitable for the investigation of new and uncertain systems, since it provides a stringent test as to the attainment of equilibrium in the system.

Finally, the advantage of the more general form of the titration-curve equation, even in the symmetrical case, is pointed out and exemplified by its application to the titrations of acidimetry and alkalimetry involving weak acids, weak bases, and their salts.

I have pleasure in thanking Messrs. F. H. Brooks and A. H. Richards for assistance in the construction of the diagrams which accompany this paper.

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# CLXXXVI.—*Colloidal Platinum. Part VII. The Effect of Electrolytes upon the Cataphoretic Velocity of Platinum Particles, and its Bearing on Stability.*

By STUART W. PENNYCUICK.

THE electric charge is being increasingly recognised as the controlling factor in the stability of hydrophobic sols. In this paper a comparative study is made of the effect of various electrolytes upon the cataphoretic velocity of platinum particles, and upon the corresponding changes in stability. Owing to the remarkable influence of traces of certain electrolytes, it is necessary to have trustworthy details regarding, first, the purity of the preparation, and secondly, the constitution of the surface ionogen whose ionisation confers the stabilising charge. From this point of view colloidal platinum is seen, from the author's previous work, to be particularly suitable. As will be shown, the velocity measurements confirm the conclusions already drawn regarding the action of acids (J., 1929, 618) and of bases (*ibid.*, p. 623) on this colloid.

The methods of obtaining the colloid charge and the electrokinetic potential are limited to observations of the electrokinetic phenomena. Of these, cataphoresis is outstanding, and accordingly considerable attention has been paid in recent years to the accurate measurement of cataphoretic velocities (see reviews by Tuorila, *Kolloid-Z.*, 1928, 44, 11, and by Pauli and Valkó, "Elektrochemie der Kolloide," Wien, 1929, pp. 149 and 202).

In this work, the author has utilised the macroscopic moving-

boundary method, as developed by Burton (*Phil. Mag.*, 1906, **11**, 436) and improved by Landsteiner and Pauli (*Verh. d. Kongr. f. innere Medizin*, XXV Kongress, Wien, 1908) and by Mukherjee (*Proc. Roy. Soc.*, 1923, *A*, **103**, 102). The technical errors arising from this method have been discussed by Mukherjee and by Kruyt and van der Willigen (*Kolloid-Z.*, 1928, **44**, 22), who have shown that extreme precautions are necessary if trustworthy results are to be obtained, and that the common practice of using, as the overlying liquid, any electrolyte having the same conductivity as the sol, is by no means satisfactory. During migration, if the colloid particles move into a slightly different environment, important changes occur which result in velocity fluctuations. It is obvious that the ideal overlying liquid would be the intermicellar fluid; Kruyt and van der Willigen (*loc. cit.*) have attempted to isolate such a liquid by subjecting portions of the sol to centrifuging and ultra-filtration, whereas Powis (J., 1916, **109**, 734) used the clear solution obtained by filtering a coagulated sol. The majority of workers, however, have been satisfied to use comparable solutions of potassium chloride or of hydrochloric acid. The author has shown (J., 1928, 2108) that, in the case of colloidal platinum, the intermicellar liquid can be isolated by freezing out the colloid particles. If this liquid is used as the overlying fluid, therefore, these particles suffer no material change in environment during the whole of their movement, and it is believed that by this device and by the exercise of the precautions now outlined, the nearest approach yet recorded to the ideal conditions has been made.

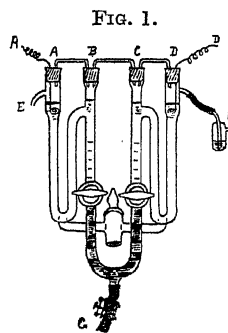
The moving boundary between the dark brown platinum sol and the clear overlying liquid is well defined, and can be followed with accuracy.

#### EXPERIMENTAL.

The mode of preparation of a sol has a direct influence on its charge and on its cataphoretic velocity. Accordingly, the various samples of colloidal platinum were prepared in exactly the same way (*Australian J. Exp. Biol. Med. Sci.*, 1927, **4**, 99), the following being the details: voltage 200, current 3.5 amps., sparking time (continuous) 18 minutes per 500 c.c. of water. After preparation, the sol was boiled for 25 minutes and stored for two days. The samples used had specific conductivities ( $\kappa$ ) ranging from 10 to 15 gemmhos (see Table I).

For the measurement of cataphoretic velocities, a modified Landsteiner-Pauli apparatus was used throughout. It was thoroughly cleaned before each determination. As the results with sodium hydroxide are of great importance, and as measurements with bases are often avoided, the method of making cataphoretic

measurements in the absence of carbon dioxide is described. Samples of the platinum sol and of the intermicellar fluid (frozen sol) are brought into two conductivity cells of low cell constant. The intermicellar fluid, which has the higher conductivity (owing to previous boiling and evaporation), is diluted with conductivity water until it shows the same specific conductivity as the platinum sol. The required amount of sodium or barium hydroxide is introduced into each cell in the absence of carbon dioxide (J., 1927, 2600), and the conductivities are brought to exactly the same values: as the platinum particles remove some of the base, the colloid solution requires more alkali than the sample of intermicellar fluid, and hence it is not sufficiently accurate simply to add equal quantities of base to the two solutions. The solutions are then introduced into the cataphoresis tube shown in Fig. 1. To keep the solutions carbon-dioxide free, the air-tight connexions *A*, *B*, *C*, and *D* are fitted. The apparatus, previously washed with conductivity water, is dried by passing a warm carbon dioxide-free air stream in at *E* and out through bubblers at *F* and *G*. The conductivity cells are fitted with tubes so that the solutions can be blown into the cataphoresis apparatus under a small head of carbon dioxide-free air. The platinum sol is introduced at *G*, until it rises 1 mm. or so above the taps, whilst the overlying solution is introduced at *E*. By careful manipulation the transference may be accomplished without any contamination whatsoever with carbon dioxide.



When acids and salts are to be used, simplifying modifications at once suggest themselves. In preparing comparable solutions in the presence of salts, the knowledge of the surface actions as previously developed (J., 1929, 618) was always utilised with the object of providing a perfectly uniform environment for the

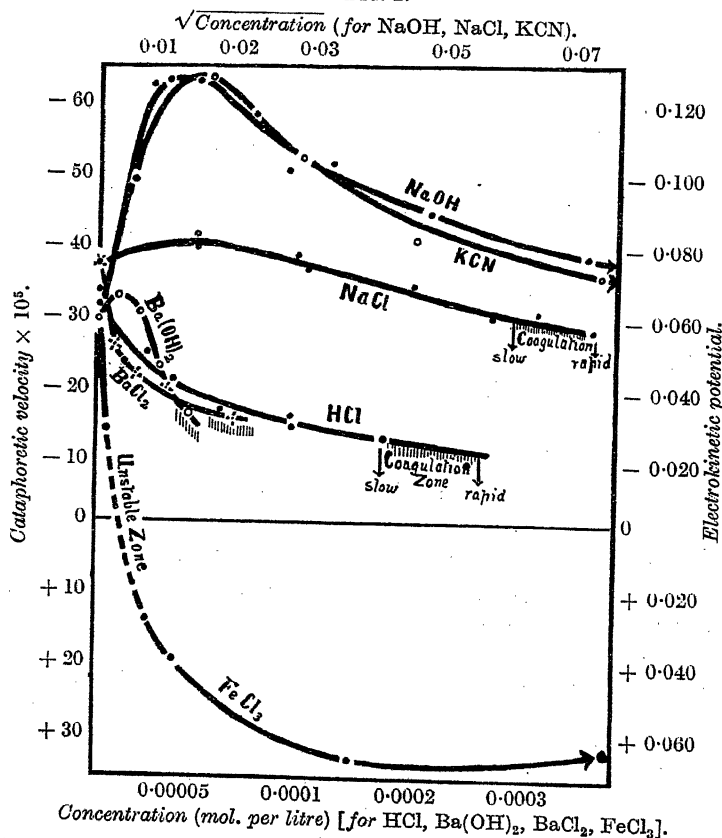
TABLE I.  
*Pure platinum sols at 25°.*

Sol.	$\kappa$ .	$[\text{H}_2\text{Pt}(\text{OH})_6]$ .	$u \times 10^5$ .	$\zeta$ .
D (unboiled) .....	5.7	$16 \times 10^{-6}$	33.3	0.062
D (boiled 25 mins.) .....	14.2	41 "	32.0	0.060
D " " .....	15.0	43 "	30.8	0.058
E (unboiled) .....	3.7	11 "	38.6	0.072
E (boiled 25 mins.) .....	11.2	32 "	37.0	0.069
F " " .....	9.7	28 "	30.7	0.057
F " " (old) .....	11.4	33 "	27.8	0.052
G (boiled 25 mins.) .....	12.0	34 "	36.4	0.068

moving particles. In all cases the solutions were prepared in the conductivity cells, and then transferred to the apparatus.

*Results.*—The distance between the electrodes was 74 cm., and the voltage 135 (less in a few cases). Each result is the average of several determinations. The error is of the order 6–7%, which is considered satisfactory for this type of measurement. Unless

FIG. 2.



otherwise stated, all velocity values recorded are negative, this sign being omitted for the sake of convenience.

The results for the pure platinum sols are set out in Table I, and curves for sols containing this and other electrolytes appear in Fig. 2.

*Interpretation of Results.*—The criticisms of McBain (*J. Physical Chem.*, 1924, 28, 706), Burton (*Colloid Symposium Monographs*, 1926, 4, 132), and Kruyt and van der Willigen (*Z. physikal. Chem.*,



1927, 130, 170) undoubtedly show that the theoretical relation between cataphoretic velocity and electrokinetic potential, which was developed some 30 years ago, rests upon very insecure grounds. Nevertheless, because of convenience and long usage, practically every investigator in this field prefers to interpret cataphoretic results in terms of electrokinetic potential  $\zeta$ .

In this paper the cataphoretic velocities ( $u$ ) themselves are recorded, and it is these which are stressed, but for the sake of comparison the  $\zeta$  values also are recorded. As colloidal platinum particles are spherical (Diesselhorst and Freundlich, *Physikal. Z.*, 1916, 17, 117), the usual Helmholtz-Smoluchowski equation,  $\zeta = 4\pi\eta u/DH$ , must be replaced by the corrected equation  $\zeta = 6\pi\eta u/DH$  (Debye and Hückel, *ibid.*, 1924, 25, 49). For the dilute solutions of electrolytes used,  $\eta$  may be taken as the viscosity of water (0.00893 at 25°), and  $D$  as 81, the dielectric constant of water;  $\zeta$  and  $u/H$  then become proportional and the equation may be written  $\zeta = (6\pi\eta/D) (u/H) = ku/H$ . In this paper  $u$  is always given as the velocity (cm. per sec.) for a potential gradient of 1 volt per cm., whence  $H = 1$ , and  $\zeta = ku$ . The value of the proportionality factor  $k$  is 187.1. The  $\zeta$  values so calculated are shown in Fig. 2 and in the table.

### Discussion of Results.

*The Pure Sols.*—The cataphoretic velocities of the pure sols, as shown in Table I, exhibit variations in spite of the similarity of the method of preparation. For the boiled sols,  $u \times 10^5$  ranges from 27.8 to 37.0 cm./sec./volt/cm. The free acid content, as obtained from the specific conductivity [assumed all to be due to  $\text{H}_2\text{Pt}(\text{OH})_6$ ], ranges from  $28 \times 10^{-6}$  to  $43 \times 10^{-6}$  equiv. The source of charge is undoubtedly the platinic acid, but it is evident from the irregularity of the figures that no simple relationship holds between cataphoretic velocity and concentration of free acid. The unboiled sols have the smallest acid content but the greatest velocities; and as the acid content increases (by boiling or ageing), the charge as revealed by cataphoretic velocity decreases. The absence of the simple relation between velocity and acid concentration which will be shown to hold for the surface-inactive acids, such as hydrochloric and nitric, is evidently due to the surface activity of the  $\text{Pt}(\text{OH})_6$  anion. An increase in the  $\text{H}_2\text{Pt}(\text{OH})_6$  concentration then has a double effect: the hydrogen ion decreases the surface ionisation, whilst the  $\text{Pt}(\text{OH})_6$  ion increases the number of surface ionogens and hence the charge. The total action is complicated by the changes in surface area, state of aggregation, etc., which must occur when the sol is boiled or aged.

The results recorded for  $u \times 10^5$  by other workers with pure platinum (Bredig) sols are 30 (Whitney and Blake, *J. Amer. Chem. Soc.*, 1904, **26**, 1339), 21 (Burton, *Phil. Mag.*, 1906, **11**, 425), 24 (Svedberg, *Nova Acta Upsala*, 1907, [IV, 2] 190), and 20–40 (Cotton and Mouton, *Compt. rend.*, 1904, **138**, 1692). Although all the results are very roughly of the same order of magnitude, variations would be expected for the reasons outlined above. (For comparison with other sols, see Pauli and Valkó, *op. cit.*)

*The Critical Potential.*—The idea that all coagulations occur at a critical potential (critical velocity) was developed by Powis (*loc. cit.*; *Z. physikal. Chem.*, 1915, **89**, 186), using oil drops and arsenious sulphide sols. The negative results of Mukherjee (*Nature*, 1928, **122**, 960), the confirmatory results of Kruyt and Briggs (*Proc. K. Akad. Wetensch. Amsterdam*, 1929, **32**, 384) and of Ghosh (J., 1929, 2693), and the indefinite conclusions of Tuorila (*Koll.-Chem. Beih.*, 1928, **27**, 44) and of Kruyt and van der Willigen (*loc. cit.*) leave the question open as to whether the critical potential has any general significance.

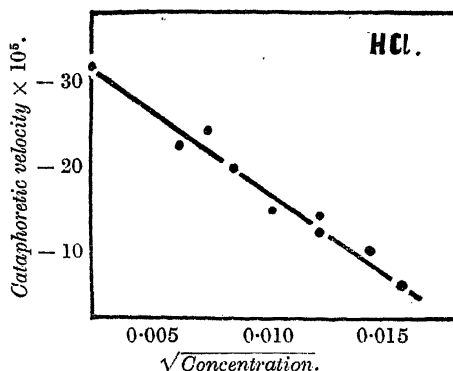
From the results now recorded, it is evident (i) that coagulation always occurs before the cataphoretic velocity has been depressed to zero, and (ii) that with hydrochloric acid, barium hydroxide, barium chloride, ferric chloride, and calcium chloride (not shown), coagulation occurs at a velocity between  $10 \times 10^{-5}$  and  $15 \times 10^{-5}$ . Hence with these electrolytes we may speak of a critical velocity (or potential). On the other hand, sodium chloride and hydroxide and potassium chloride (not shown) show coagulation velocities of quite a different order. These conclusions are in general accord with those of Powis and of Ghosh (*loc. cit.*) on arsenious sulphide, and of Freundlich and Zeh (*Z. physikal. Chem.*, 1925, **114**, 65) on both arsenious sulphide and ferric hydroxide sols. There appears to be strong evidence for the view that, with electrolytes which coagulate at low concentrations, a critical potential exists below which the sols are unstable, but that where a large concentration of electrolyte is required, coagulation occurs at a much higher potential.

*Hydrochloric Acid.*—It has been established that colloidal platinum is an acidoid sol, and that the ionisation of the surface hexahydroxyplatonic acid is the source of charge and of stability. Coagulation by surface-inactive acids, such as the common inorganic acids, is then interpreted as due to the repression of the surface ionisation or of the ionic double layer. The slope of the hydrochloric acid curve (Fig. 2) is in keeping with this view. Further confirmation is at hand, for, by the application of the Debye-Hückel theory (*Physikal. Z.*, 1923, **24**, 185), it follows that

if no abnormalities occur, the addition of an electrolyte should cause a decrease in the velocity which is directly proportional to the square root of the concentration, and actually when these two variables are plotted against one another, the curve (Fig. 3) shows that the linear relationship holds.

These conclusions are in agreement with the results obtained with the acidoid mastic sol, where it has been shown that coagulation by inorganic acids is a plain case of ionic repression (Michaelis, "The Effect of Ions in Colloidal Systems," 1925, 67).

FIG. 3.



*Barium Chloride.*—On the addition of this salt, the cataphoretic velocity decreases rapidly, and coagulation occurs at a relatively low concentration. Here the outstanding action, and the one which ultimately leads to coagulation, is the ionic exchange of hydrogen contra-ions for barium ions from solution. Because of this interfering action, the velocity- $\sqrt{\text{concentration}}$  curve does not yield a straight line.

The critical potential for this and comparable salts lies between  $-0.020$  and  $-0.030$  volt. The corresponding value of  $\zeta$  recorded by Powis for oil drops and arsenious sulphide is  $-0.025$  volt.

*Sodium Hydroxide.*—From a study of the reactions of colloidal platinum in basic solutions (J., 1929, 623), the author has concluded that univalent bases have the important property of reacting with surface non-ionogenic groups (probably oxides) to form further stabilising ionogens. It was, in fact, in order to test this conclusion that the present experiments were undertaken. The remarkable increase in the cataphoretic velocity on the addition of sodium hydroxide completely confirms the view that fresh surface ionogens are formed. From the curve in Fig. 2 (where, for convenience, the concentration is replaced by its square root),

it is seen that when  $5.3 \times 10^{-6}$  equiv. of base has been added (free sodium hydroxide =  $33 \times 10^{-6}$  equiv.), the cataphoretic velocity is more than doubled; on further addition of base, the velocity remains practically constant over a considerable range; and at higher concentrations it begins to decrease. The important stabilising and peptising action of univalent bases is undoubtedly connected with this increase in charge. The flat maximum in the curve is probably related to the view (Hevesy, *Kolloid-Z.*, 1917, 21, 129) that the electrokinetic potential of colloid particles cannot exceed a certain maximum, viz., approx. 0.105 volt ( $0.070 \times 3/2$ ). At all events the very high value of  $\zeta$  here obtained, 0.120 volt, is not exceeded by any other colloid system.

The important charging action of the hydroxyl ion was first emphasised by Perrin (*J. Chim. physique*, 1904, 2, 601), and has since been demonstrated for various negative suspensions—for emulsions by Ellis (*Z. physikal. Chem.*, 1912, 78, 321; 80, 597), and for kaolin by von Buzágh (*Kolloid-Z.*, 1929, 48, 33) and Dubrissay, Trillat, and Astier (*Compt. rend.*, 1929, 189, 41). These workers all find an increase in  $\zeta$  on the addition of univalent bases. The explanation in terms of an increase in surface ionogens can be extended to include all the known observations. The streaming potential against ordinary glass shows no such maximum (Ellis, *loc. cit.*; Powis, *Z. physikal. Chem.*, 1915, 89, 91; Elissafoff, *Z. physikal. Chem.*, 1912, 79, 385): the high initial  $\zeta$  indicates that the sodium hydroxide from the hydrolysis of the sodium silicate has already given the glass its maximum charge.

The cataphoretic velocity of the platinum particles at the coagulation point (in the case of sodium hydroxide) is remarkably high, viz.,  $36.8 \times 10^{-5}$  ( $\zeta = 0.069$ ), i.e., higher than the initial velocity of the particles. Sodium hydroxide coagulation figures for other acidoid sols have not yet been recorded.

*Barium Hydroxide.*—On the addition of barium hydroxide, the cataphoretic velocity shows an extremely small initial increase, in striking contrast to the results obtained with univalent bases. This small increase cannot be ascribed to the lack of formation of surface ionogens, for it has been shown that platinum sols take up 4 or 5 times as much barium hydroxide as sodium hydroxide. There is little doubt that both the low value of the maximum and the subsequent rapid decrease in the cataphoretic velocity are intimately connected with the strong inter-attractive forces between the colloid particle and the ion of higher valency. This, in fact, is the interpretation of the "valency rule."

The shape and the position of the curve show that the charging

and stabilising action of the hydroxyl ion are here very soon outweighed by the coagulating action of the bivalent barium ion. Barium hydroxide will therefore have no pronounced action as a peptising agent.

The only example in the literature where a similar maximum for a bivalent base is recorded is that of Dubrissay, Trillat, and Astier (*loc. cit.*) for kaolin.

*Sodium Chloride.*—Sodium chloride and also potassium chloride show two interesting features: a definite maximum in the velocity-concentration curve, and an abnormally high velocity at coagulation. Similar maxima for univalent salts are recorded by Ivanitzkaja and Proskurnin for colloidal arsenious sulphide and vanadium pentoxide (*Kolloid-Z.*, 1926, **39**, 15), by Thiessen and Heumann for gold (*Z. anorg. Chem.*, 1929, **181**, 379), and by Powis for oil emulsions (*loc. cit.*). They are generally interpreted in terms of the charging action (adsorption) of the negative ion, usually the chlorine ion. In the case of colloidal platinum, the results with hydrochloric acid show that this ion is not surface-active, and there is no reason to believe that such activity would develop in the case of its salts. The author considers that the explanation of the initial increase in the cataphoretic velocity is to be found in the hydrolytic cleavage of the salt. The collective evidence for this view is shortly to be presented elsewhere.

The high velocity at coagulation, *viz.*,  $25 \times 10^{-5}$  ( $\zeta = 0.050$ ), is not unique. Similar high values for univalent salts have been recorded with colloidal arsenious sulphide (Freundlich and Zeh; Powis; Kruyt and van der Willigen; *loc. cit.*), and also for oil emulsions (Limburg, Dissertation, 1924). Owing to the low platinum content, the salting-out effect suggested by Powis has in this case little significance; and there is nothing in the records to indicate, as suggested by Kruyt and van der Willigen, that variations in the dielectric constant of such a weak electrolyte as 0.005*N*-sodium chloride would play an interfering part.

*Potassium Cyanide.*—The potassium cyanide curve corresponds very closely to that of a univalent base. Owing to the very high hydrolysis of this salt the result is not surprising. The hydrolysis is doubtless increased by the removal of some potassium hydroxide by the platinum surface, and here we have a rather obvious, but extreme case of hydrolytic cleavage. The well-known surface activity of the cyanide ion may also play some part. It will be noticed that the maximum electrokinetic potential for sodium hydroxide (0.120 volt) is not exceeded.

*Ferric Chloride.*—Ferric chloride shows a first coagulating zone when the negative velocity is decreased to about  $-12 \times 10^{-5}$

cm. per sec., and the sol then remains unstable over a range of ferric chloride concentration, but when this reaches  $0.00004M$ , and the velocity becomes  $+15 \times 10^{-5}$ , the charge is reversed and the sol again becomes stable. For higher saline concentration, well above  $0.004M$ , the sol behaves as a typical positive sol. The existence of an unstable zone and of a negative and a positive critical potential are clearly shown by the curve.

*Coagulation Zones.*—The shaded portions of the various curves represent the coagulation zones, i.e., the concentrations between slow and rapid coagulation. It has been usual to distinguish between two critical potentials, one for slow and one for rapid coagulation, and to assume that, whilst the former may have a relatively large value, the latter is approximately zero. The slopes of the curves at and near coagulation show that this is not the case, but that the potential at rapid coagulation is only slightly less than that at slow. This is confirmed by the actual measurements. The velocity at slow coagulation is obtained in the normal manner, the experiment being completed before the particles have had time to coalesce; and that at rapid coagulation can also be directly measured if the necessary amount of salt, and no more, is added. For example, if a sol is made  $101 \times 10^{-6}M$  with respect to barium chloride, an extremely fine but quite definite precipitate can be noticed with a magnifying glass. This settles so very slowly that its cataphoretic velocity may be measured in the normal manner. The final point on the barium chloride curve was obtained with such a coagulated sol. The settling cannot altogether be neglected, and therefore such values are, if anything, a little too low. The fact that such points fall in the continuation of the curves brings out the interesting feature, viz., that the coagulated agglomerates move with the same velocity (and therefore have the same potential) as the individual particles immediately before coalescence.

*The Cause of Coagulation.*—The recognition of colloid particles as great multivalent ions was first emphasised by Billiter (*Z. physikal. Chem.*, 1903, 45, 307) and Duclaux (*J. Chim. physique*, 1907, 5, 29); but the practical demonstration that colloid systems are strong electrolytes is due to the work of Pauli and of Bjerrum (*Z. physikal. Chem.*, 1924, 110, 656). In the light of this view, the condensed double layer of Helmholtz, Lamb, and Smoluchowski has become replaced by the diffuse double layer or ionic atmosphere of Gouy (*J. Physique*, 1910, 9, 457) and of Debye and Hückel (*loc. cit.*). Accordingly, the source of colloid stability is the ionisation of the surface ionogens, whose contra-ions ("gegenionen") extend into the solution as an ionic atmosphere. Any

increase in the ionic concentration, *e.g.*, on addition of acids to acidoid sols, causes an attenuation of the ionic atmosphere, or a displacement of the "electrical centre of gravity" of the contractions towards the colloid surface. The cataphoretic velocity and the electrokinetic potential are accordingly decreased, and at some critical value coagulation ensues. If there be no interfering reactions, the Debye-Hückel theory requires that the average density of the ionic atmosphere be proportional to the square root of the concentration of coagulating ion, and in the simplest cases this has been confirmed. With all salts, however, the kationic interchange is superimposed on the above relation, and the simple linear law does not hold. With univalent bases the production of fresh surface ionogens acts in the opposite direction to the effect due to the increase in concentration of the contra-ions; hence the maximum in the curve. For these cases the complete relation between cataphoretic velocity and electrolyte concentration is still lacking. The valency rule is also directly interpreted in terms of the theory.

Any decrease in the cataphoretic velocity leading to coagulation has usually been explained in terms of the "adsorption" of the oppositely charged ion, but, although this hypothesis has been of service, ultimately it will have to be abandoned, for it fails to explain even the simplest case, *viz.*, the coagulation of an acidoid sol by an acid, the work with platinum (and also with mastic) having shown that the colloid particles do not remove (or adsorb) any of the coagulating acid. Where other ions, *e.g.*,  $\text{Ba}^{++}$ ,  $\text{Al}^{+++}$ , are the active coagulating agents, the more definite explanation in terms of ionic interchange is to be preferred.

In spite of numerous speculations, we have no complete answer to the question, "Why does coagulation ensue before the colloid is completely discharged?" The work with colloidal platinum shows that there are no abrupt changes (beyond instability) at the coagulation point. This has also been emphasised by Ellis and by Powis with oil emulsions. We can only assume that, when the ionic atmosphere has been sufficiently attenuated, the repulsion which existed when the two particles approached under their Brownian movement is no longer sufficient to keep them from adhering. The latter effect is probably largely a capillary one, and is not solely due to changes in interfacial tension, as is often supposed. Perrin's work with mastic and gamboge, and that of Ellis and of Powis with oil emulsions, shows that at coagulation the droplets do not run together but adhere in clusters. Peptisation experiments with platinum are in accord, for on addition of sodium hydroxide to a sol which has been coagulated

with sodium chloride, peptisation follows readily, and no severe treatment is necessary to draw the adhering particles apart.

### *Conclusion and Summary.*

Colloidal platinum is a typical hydrophobic acidoid sol. In the presence of air, the surface appears to contain oxide and acid only.

The changes in the cataphoretic velocity of the particles have been measured in the presence of certain electrolytes.

The effect of inorganic acids is interpreted as a direct repression of the diffuse ionic atmosphere, and the linear relation of Debye and Hückel is found to hold.

Univalent bases react with the surface oxide to form fresh stabilising ionogens, and the cataphoretic velocity accordingly passes through a maximum. Bivalent bases show a very weak maximum.

Hydrochloric acid, barium hydroxide, and barium, calcium, and ferric chlorides show a critical velocity and critical potential.

Poor coagulants, such as univalent salts and univalent bases, show a maximum in the velocity-concentration curve, and an abnormally high velocity (and potential) at coagulation.

Ferric chloride shows two critical velocities, one negative and the other positive.

The coagulation process in the presence of electrolytes is discussed in terms of the results obtained.

The author wishes to record his indebtedness to the Trustees of the Endowment Fund of the Council for Scientific and Industrial Research of the Commonwealth of Australia for grants towards the purchase of platinum used in this series of investigations.

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## CLXXXVII.—*A Simple Electrically Controlled Thermostat.*

By JOHN ARNOLD CRANSTON.

THIS thermostat is of a type that has been in use for a number of years in this laboratory, and as it has certain advantages in respect of compactness and economy in use of electric current, a description of it seems desirable.

The vessel (Fig. 1) consists of a glass accumulator jar,  $40 \times 28 \times 22$  cm., of 25 litres capacity; it is divided into two approxi-



mately equal portions by a glass plate, *E*, which is suspended from its sides and serves to improve the efficiency of stirring by directing the flow of the water from the stirrer into a one-way stream round the tank. Water is kept in the vessel to a level some 2 cm. above this plate.

The rear portion of the vessel contains (i) a heating lamp *D*, of the Robertson radiator type consuming 1 amp. at 250 volts,

FIG. 1.

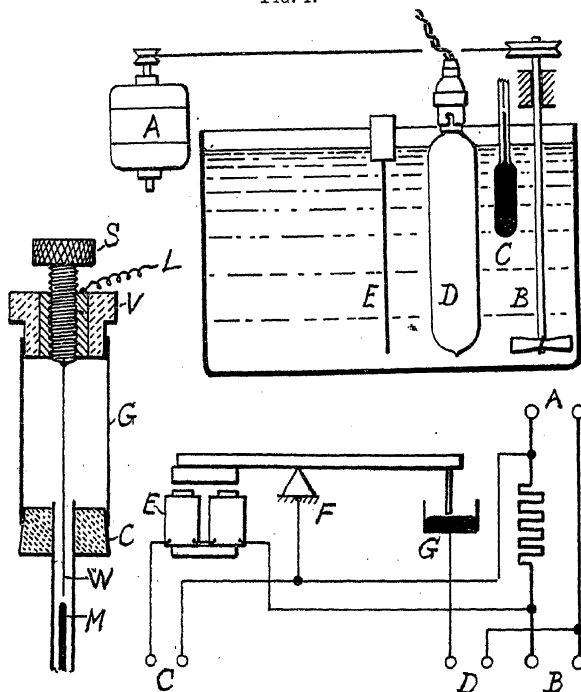


FIG. 2.

FIG. 3.

(ii) a stirrer *B*, consisting of a monel metal propeller mounted on a shaft which is connected to a bicycle hub and driven by an electric motor or hot-air engine *A*, (iii) a thermoregulator *C*, consisting of a bulb with a capillary stem. A piece of platinum wire, sealed into the bulb, enables electrical contact to be made with the mercury within. A piece of nichrome wire, *W* (Fig. 2), acts as the other terminal of the circuit and makes and breaks contact with the surface of the mercury *M* in the capillary tube. The wire is soldered to the base of the screw *S*, which is in electrical

contact with the lead-in wire *L*. The screw is mounted in a vulcanite cap *V*, supported by a glass tube *G* and rubber cork *C*. By means of this screw, contacts may be set to operate at any desired temperature.

The thermoregulator circuit includes a coil of wire *E* (Fig. 3) of the electric-bell type, above which is suspended a piece of soft iron attached to the lever arm of a balance; when expansion of mercury in the capillary tube closes this circuit, the current flowing through the coil attracts the soft iron and so draws the other lever arm out of a trough of mercury *G*, thus breaking the main circuit of the heating lamp. The regulator circuit requires a low-voltage current, which is obtained by inserting a piece of nichrome wire of about 7 ohms resistance in the main circuit driving the motor stirrer, and by tapping the current from the ends of this wire. A convenient form of resistance is the wireless rheostat.

If it is desired to maintain the temperature constant for an experiment lasting several weeks, and the circumstances are such that a single failure in the make-and-break system, with its consequent rise in temperature, would ruin the experiment, the following precaution can be adopted. A second thermoregulator can be inserted in parallel with the first, but set to operate at a slightly higher temperature than the desired one.

Since a continuous flow of electric current is necessary to operate the thermoregulator, economy of current is effected by using it to drive the motor instead of having a lamp in circuit providing useless illumination.

The electrical connexions are shown diagrammatically in Fig. 3; an ordinary electrical wall block, 9"  $\times$  9", is used for mounting (i) all the required terminals, (ii) the make-and-break of the heating circuit, (iii) the shunt for the low-voltage current supply, and (iv) two condensers of about 0.5 microfarad capacity each. These are inserted to minimise the sparks in the two make-and-break circuits.

A test with a Beckmann thermometer showed the variation of temperature at 25° to be 0.03°.

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CLXXXVIII.—*The Constitution of Some Organic Derivatives of Thallium.*

By NEVIL VINCENT SIDGWICK and LESLIE ERNEST SUTTON.

THE majority of the known metallic alcoholates are salt-like substances; they are non-volatile, insoluble in organic solvents such as benzene, and they often combine with the parent alcohol. Examples of this type are the alcoholates of the alkali metals, the alkaline-earth metals (Chablay, *Compt. rend.*, 1911, **153**, 953; de Forcrand, *ibid.*, 1912, **154**, 1441; Doby, *Z. anorg. Chem.*, 1903, **35**, 93), zinc, magnesium (Tolkatscheff, *J. Russ. Phys. Chem. Soc.*, 1901, **33**, 469; Szarvasy, *Ber.*, 1897, **30**, 806), and lead (Chablay, *loc. cit.*). Aluminium is exceptional in that, though its methoxide decomposes on heating, its ethoxide melts at 135° and boils at 234—235°/23 mm., the propoxide and the amyloxyde being similar (Hillyer, *Amer. Chem. J.*, 1897, **19**, 597; Hillyer and Crooker, *ibid.*, p. 37). With the exception of the methoxide these may be regarded as esters of aluminic acid and as being analogous to the esters of boric acid.

Thallos ethoxide belongs to neither of these types; it is a colourless oil at room temperature (m. p. -3°) which is miscible with benzene, only partially with ethyl alcohol, but has no appreciable vapour pressure at temperatures up to 80°, where it decomposes. It is readily decomposed by water or carbon dioxide. The *n*-propoxide, the *n*-butoxide, and the isobutoxide have also been made and appear to be of the same type (Lamy, *Ann. Chim. Phys.*, 1863, **67**, 395; 1864, **3**, 373; Kahlbaum, Roth, and Siedler, *Z. anorg. Chem.*, 1902, **29**, 177), but the methoxide and cyclohexanyloxyde (Lamy, *loc. cit.*; de Forcrand, *Compt. rend.*, 1923, **176**, 20) are white microcrystalline solids which do not melt, but decompose above 110°. The phenoxide (de Forcrand, *loc. cit.*) and some of the substituted phenoxides (Christie and Menzies, *J.*, 1925, **127**, 2373) are stable white solids which can be recrystallised from water and have definite melting-points, but are soluble in benzene (see later), while the ethylene glycolate and glycerate (de Forcrand, *loc. cit.*) are yellow crystalline solids. It therefore seemed that some, at least, of these alcoholates were covalent, but, from their non-volatility, were associated.

In the present investigation, the molecular weights of the methoxide, the ethoxide, the cyclohexanyloxyde and the benzyloxyde in benzene solution were determined at the freezing point, those of the methoxide and the ethoxide also being determined in their parent alcohols at the boiling points. In addition, the molecular weights of several phenoxides and of ethyl thalioacetoacetate were measured

in boiling benzene, while finally the solubilities of the ethoxide in ethyl alcohol and of the methoxide in methyl alcohol and in benzene were determined.

### EXPERIMENTAL.

*Preparation of Materials.*—*Thallous ethoxide.* This was the starting material for all the thallium derivatives used. Some of it was very kindly supplied to us by Dr. R. C. Menzies and more was made by Lamy's method in an apparatus similar to one described to us by Dr. Menzies, wherein thallium, rolled into ribbon, was subjected to the combined action of boiling, dry ethyl alcohol and dry oxygen. The thallous ethoxide dropped into the ethyl alcohol as it was formed, being subsequently withdrawn and filtered through a plug of cotton-wool into a receptacle. It kept best if a layer of alcohol was allowed to remain over it but, in any case, it decomposed in time with the formation of a black colloidal precipitate which could not be removed by filtration. We found that it could then readily be purified by dissolving it in boiling, dry ethyl alcohol, filtering the solution and allowing it to cool, and separating the two liquid layers. Specimens so purified kept considerably better than the crude ones. Ethyl alcohol is soluble in the ethoxide, though only to a small extent (Lamy, *loc. cit.*), so the last traces of it were removed from small quantities of ethoxide, as required, by keeping them for 24 hours over metallic sodium in a vacuum desiccator.

*Thallous methoxide.* This was prepared as described by de Forcrand (*loc. cit.*) by double decomposition between the ethoxide and an excess of dry acetone-free methyl alcohol (kindly supplied by the Balliol and Trinity College Laboratories). Owing to its instability, small quantities were made as required and purified by recrystallisation from dry benzene. The time during which the filtered solutions were exposed to the air was kept as short as possible, and, with care, specimens could be obtained which gave very clear benzene solutions in the molecular-weight determinations. When quite free from methyl alcohol, the methoxide was very unstable; these solutions would begin to deposit a black precipitate even at 25–30°.

Thallous methoxide has no melting point; the solid begins to decompose above 120°.

*Thallous cyclohexanyloxide.* This was prepared in a similar way, thallous ethoxide being added to an excess of a dry, ethereal solution of cyclohexanol which had twice been distilled in a vacuum to remove most of the water in it. It was washed with a small quantity of pure dry ether and recrystallised from benzene. It has no melting point, but begins to decompose above 110°.

*Thallous benzyloxyde* was also prepared in this way, but, owing to its greater solubility in ether, the reaction mixture was well cooled in a freezing-bath. The product crystallised in colourless shining plates, which were filtered off, washed with a small quantity of well-cooled ether, and kept over potash. It was finally recrystallised from ligroin (b. p. 60—80°). The removal of the last traces of benzyl alcohol from small samples of this substance was difficult, owing to the limited solubility in ligroin of the alcohol and the relatively great solubility of the benzyloxyde.

This compound, m. p. 74—78°, has not been previously described. It decomposes slowly on keeping, is very sensitive to moisture, and is readily soluble in benzene or ether [Found: Tl, estimated as iodide, (1) 65.9, (2) 65.1.  $C_7H_7OTl$  requires Tl, 65.6%].

Dr. T. V. Barker and Mr. R. C. Spiller kindly made a micro-crystallographic examination of this substance. The crystals were regular octagonal plates which, under crossed Nicols, exhibited straight extinction. Normal to the plate was the acute bisectrix of a positive biaxial figure with medium axial angle. The system was possibly orthorhombic, certainly not cubic, tetragonal, hexagonal or rhombohedral.

*Thallous phenoxide, m-tolyloxyde, o-methoxyphenoxide, m-methoxyphenoxide, thallous salicylaldehyde, and the thallous derivative of o-vanillin.* These were all made by double decomposition of the ethoxide with an excess of an ethereal solution of the appropriate phenol. They were filtered off, washed with ether, and recrystallised by solution in either boiling benzene or pyridine and precipitation with ligroin (b. p. 60—80°). The m. p.'s of the first five substances were higher than those reported by Menzies and Wilkins (J., 1924, 125, 1148) and Christie and Menzies (*loc. cit.*), who recrystallised them from alcohol or water.

Thallous phenoxide .....	M. p. 233—235° (C. & M., 231—235°)	
„ <i>m</i> -tolyloxyde .....	196°	(187°)
„ <i>o</i> -methoxyphenoxide .....	164°	(160°)
„ <i>m</i> -methoxyphenoxide .....	148°	(146—148°)
„ salicylaldehyde .....	197° decomp.	(186°)
„ <i>o</i> -vanillin ..	142° decomp.	

The last compound is new. After purification it was obtained as fine yellow crystals which kept well (Found: Tl, determined as iodide, 58.2.  $C_8H_7O_3Tl$  requires Tl, 57.5%); the crude product eventually turned brown or black. It was sufficiently soluble in boiling benzene for its molecular weight to be determined (thallous salicylaldehyde is not).

*Determination of Molecular Weights in Benzene by the Beckmann Freezing-point Method.*

For these determinations the solvent had to be thoroughly dry and the solutions had to be protected against wet air during the course of the experiments, owing to the ease of hydrolysis of the solutes.

The benzene was purified in the usual manner, by repeated fractional freezing and by shaking with sulphuric acid. It was distilled, in a stream of dry air, into a reservoir from which, by the closing of an air by-pass tap, it could be blown direct into the Beckmann tube. Throughout the experiment a slow stream of dry air was passed. It left the apparatus through the stirrer sleeve, which was provided with the usual buffer space to prevent wet air being drawn in by the movement of the stirrer. The air appeared to be sufficiently saturated with benzene in passing through the distilling flask, for no drift of readings, which could be ascribed to evaporation of benzene from the Beckmann tube, was observed. The efficiency of the apparatus in this form was once tested by observing the freezing point of some benzene over a period of 6 hours. The first and the last reading differed by  $0.003^{\circ}$ , the former being  $0.001^{\circ}$  above and the latter  $0.002^{\circ}$  below the mean of the whole series. In view of this and the fact that the alcoholates gave perfectly clear solutions, the drying was considered satisfactory.

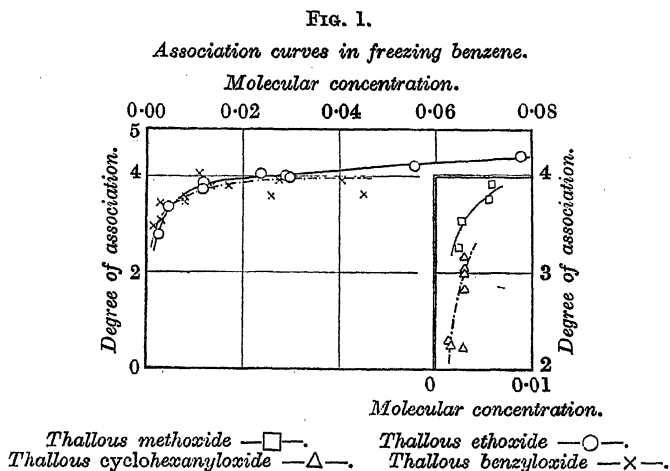
Since the methoxide and the *cyclohexanyloxyde* gave maximum lowerings of only  $0.08^{\circ}$  and  $0.05^{\circ}$  respectively, considerable care was necessary in working with them. Whenever possible, freezing-point readings were taken until four successive values differing by not more than  $0.005^{\circ}$  had been obtained, and the mean value taken. If greater fluctuations persisted, the mean of six readings was taken.

We confirmed the observation of Jones and Bury (J., 1925, 127, 1947) that dry benzene is difficult to supercool, and, moreover, at first we experienced difficulty in avoiding caking of the fine benzene crystals on the walls of the tube. This occurred less in the case of the solutions than with the pure solvent, so the conditions under which the "convergence temperatures" (Wildermann, *Proc. Roy. Soc.*, 1896, 59, 251) were reached were different in the two cases, and a zero error resulted. This difficulty was overcome by using an air space round the Beckmann tube of at least 8 mm. and by supercooling about  $1^{\circ}$  for all readings.

The methoxide, ethoxide, or *cyclohexanyloxyde* was introduced through the side tube of the Beckmann apparatus, and, after the readings had been taken, some of the solution was withdrawn through a curved tube which was passed through the side tube,

filtered through a plug of cotton-wool, weighed, and then shaken with a definite volume of water, which was shown to remove the whole of the thallium. The concentration of the solution in the Beckmann tube was altered by adding more benzene from the reservoir to make it up roughly to its original volume, and the cycle of operations repeated. The thallous hydroxide in the aqueous layers was titrated with *N*/50-hydrochloric acid (methyl-red indicator) and the concentration of the original benzene solution could then be calculated. The benzyloxyde was weighed into the Beckmann tube.

The degrees of association of the thallous compounds were calculated (the cryoscopic constant of the benzene being taken as 53.1



from the results of calibration experiments with naphthalene as solute) and plotted against the "simple molecular concentrations," *i.e.*, the quotient of the weight of solute per 100 g. of solvent divided by its simple molecular weight. The curves obtained are shown in Fig. 1 and the data from which they are constructed are tabulated below. The error in the associations of the sparingly soluble substances could be expected to be 5%, allowing an error of 0.002° in the depression of freezing point and of 0.05 c.c. in the titrations. For most points it is actually less.

*Molecular Weights in Benzene, Ethyl and Methyl Alcohols by the  
Cottrell-Washburn Boiling-point Method.*

The apparatus used for the measurements with benzene and ethyl alcohol was an adaptation of that described by Cottrell (*J. Amer. Chem. Soc.*, 1919, 41, 721; see also Washburn, *ibid.*, p. 729) so designed

TABLE I.

$dT$ , obs.	G. solute per 100 g. solvent.	Simple mol. conc.	$M$ .	Assocn.
Thallous ethoxide.				
0.3095°	5.90	0.0237	1011	4.06
0.160	2.92	0.0117	987	3.88
0.070	1.105	0.00444	837	3.36
0.379	7.14	0.0287	999	4.01
0.165	2.905	0.0117	933	3.745
0.048	0.628	0.00252	694	2.735
0.924	19.32	0.0776	1108	4.45
0.690	13.78	0.05535	1058	4.25
0.396	7.41	0.02975	992	3.98
Thallous methoxide.				
0.076	1.27	0.00540	887	3.775
0.0385	0.603	0.002565	833	3.545
0.078	1.335	0.00568	907	3.86
0.038	0.550	0.00234	767	3.265
Thallous cyclohexanyloxide.				
0.050	0.869	0.00287	921	3.04
0.048	0.867	0.00286	957	3.16
0.040	0.5055	0.00229	670	2.21
0.050	0.8535	0.002815	905	2.985
0.037	0.475	0.00157	681	2.245
0.032	0.4175	0.00138	692	2.283
0.054	0.872	0.00288	856	2.825
Thallous benzyloxide.				
0.024	0.416	0.00138	918	2.95
0.052	0.938	0.00302	956	3.075
0.119	2.431	0.00782	1083	3.483
0.043	0.862	0.00277	1062	3.415
0.118	2.464	0.00793	1170	3.56
0.235	5.243	0.0169	1183	3.805
0.183	4.079	0.0131	1181	3.800
0.379	8.018	0.0258	1121	3.604
0.658	13.98	0.04495	1126	3.62
0.142	3.39	0.0109	1265	4.06
0.369	8.515	0.0274	1223	3.93
0.538	12.45	0.0405	1226	3.94

that the solutions could be kept dry. The dry solvent was distilled in a stream of dry air into a reservoir from which it could be elevated into a burette, as required, by suction, and it could be run out from this direct into the actual boiling-point apparatus. A side tube, from the outlet, was connected with this so that a positive pressure of dry air could be maintained within it, but no stream of air went through. The end space of the burette was calibrated in order that it could be completely emptied, and risk of solvent slowly leaking through the tap, which could not be greased, was thus avoided. The actual boiling-point apparatus is shown in Fig. 2. The outer Pyrex tube was 5 cm. in diameter at the top, but only 2.5 cm. at the



bottom, in order to use less liquid. The cork A carried a Beckmann thermometer, B, the end of the burette, C, the leads to the spiral composition-tubing condenser, D, and the pressure supply tube, E. There was also a hole through which solution could be withdrawn. An inner tube, F, 2.5 cm. in diameter, slightly constricted at the bottom, was held on to the thermometer by means of a cork, and the Y-tube G, through which the mixture of liquid and vapour rose, rested on this constriction and was held central by a loop of nickel wire encircling the thermometer. The dimensions are important, and the diagram is therefore drawn to scale. Radiation, etc., was prevented by the asbestos jacketing, and the burner was shielded from draughts by a mica chimney.

The results of two trial runs with ethyl alcohol as solvent and benzil as solute are in Table II. The readings were steady to  $0.001^\circ$  and it will be seen that the method is satisfactory for elevations down to  $0.02^\circ$ .

For the ethoxide, as in the freezing-point measurements, successive solutions were made up in the tube, their boiling points were determined, and they were then withdrawn and analysed. The more stable phenoxides could be weighed into measured volumes of benzene.

The ethyl alcohol was first dried with quick-lime and then with calcium; the benzene was treated as before.

FIG. 2.

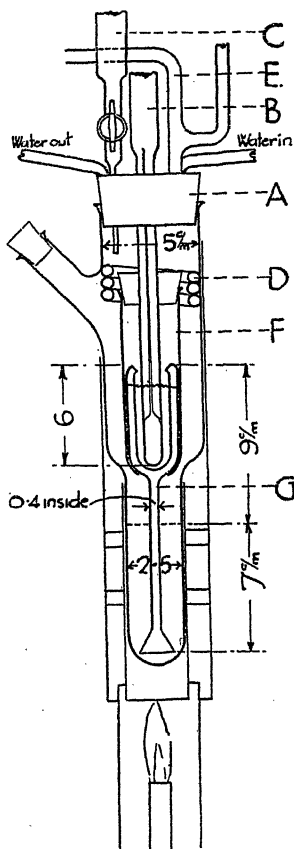


TABLE II.

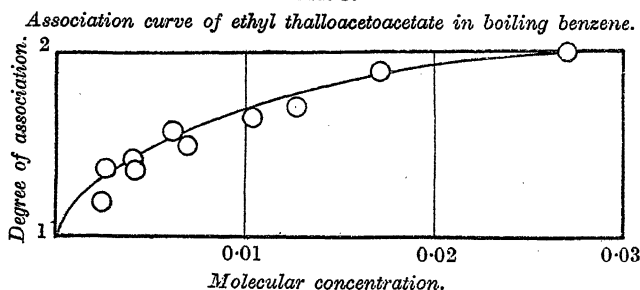
$dT$ , obs.	G. solute per 100 g. solvent.	Ebullioscopic const.	$dT$ , obs.	G. solvent per 100 g. solvent.	Ebullioscopic const.
0.021°	0.3805	11.59	0.041°	0.764	11.27
0.052	0.9930	11.00	0.069	1.261	11.50
0.101	1.920	11.05	0.104	1.914	11.41
0.173	3.230	11.25	0.147	2.735	11.29

Methyl alcohol rapidly attacked the corks in the above simple type of apparatus, so an all-glass apparatus, similar to that of

Washburn (*loc. cit.*), originally designed for use with pyridine, was adapted for use with this solvent. The dimensions were essentially the same as in the other apparatus, the inner tube fitted into the outer one by means of a large ground joint, the thermometer was fixed in it by a small piece of rubber tube, and the Y-tube rested on two pairs of indentations and was kept central by a loop of wire, as before. It had a side tube with a condenser jacket, and the end of this was connected with the dry air supply, so that a small pressure could be maintained within the apparatus.

The methyl alcohol was supplied by the Balliol and Trinity College Laboratories and was dried with aluminium methoxide (from aluminium amalgam); the thalious methoxide was freshly made, and not recrystallised from benzene. The general procedure was like that for the ethoxide, the solutions being poured out through a small side tube after the boiling point had been determined.

FIG. 3.



The degrees of association are tabulated below, and those for ethyl thalloacetoacetate are shown, plotted against simple molecular concentration, in Fig. 3.

TABLE III.

*Molecular Weights in Ethyl Alcohol.*

$dT$ , obs.	G. solute per 100 g. solvent.	Simple mol. conc.	$M$ .	Assoen.
Thalious ethoxide.				
0.140°	13.08	0.0526	1065	4.28
0.066	5.15	0.0207	890	3.57
0.040	2.65	0.0106	755	3.03
0.113	9.09	0.0365	917	3.685
0.116	9.79	0.0393	963	3.865
0.079	6.14	0.0247	887	3.56
0.039	2.86	0.0115	836	3.36
0.156	13.69	0.0550	1000	4.02
0.083	5.63	0.0226	774	3.11
0.036	2.88	0.0116	912	3.66
0.018	1.52	0.0061	966	3.88

(Ebullioscopic constant taken as 11.4, mean value from Table II.)

*Molecular Weights in Methyl Alcohol.*

## Thallous methoxide.

0.076	1.59	0.0068	186.5	0.79
0.088	2.043	0.0087	206.5	0.88
0.062	1.96	0.0083	281	1.20
0.080	2.07	0.0088	230.5	0.98

(Ebullioscopic constant taken as 8.9, mean of values in "Physikalische-Chemische Tabellen," Landolt-Börnstein.)

*Molecular Weights in Benzene.*

## Thallous phenoxide.

0.029	1.124	0.00378	1091	3.67
0.055	2.226	0.00749	1139	3.835
0.025	0.762	0.00257	858	2.89
0.048	1.288	0.00434	755	2.54
0.060	1.680	0.00566	787	2.65

Thallous *o*-methoxyphenoxide.

0.026	1.113	0.00340	1223	3.74
0.045	1.900	0.00581	1188	3.63
0.080	3.650	0.01116	1283	3.92
0.135	5.910	0.01840	1232	3.77
0.036	1.818	0.00555	1420	4.34
0.055	2.672	0.00815	1367	4.17
0.086	4.075	0.01243	1333	4.07
0.123	5.490	0.01678	1256	3.84

Thallous *m*-methoxyphenoxide.

0.032	1.504	0.00460	1321	4.04
0.064	3.952	0.0121	1321	4.04
0.111	5.290	0.0162	1338	4.09
0.053	2.400	0.00734	1279	3.90
0.112	4.285	0.0131	1076	3.29
0.138	5.430	0.0166	1105	3.375

Thallous *o*-vanillin derivative.

0.041	1.639	0.00463	1124	3.18
0.050	2.385	0.00674	1340	3.78
0.085	3.565	0.01007	1180	3.33

## Ethyl thalloacetoacetate.

0.055	0.864	0.00259	442	1.37
0.080	1.335	0.00401	469	1.41
0.109	2.028	0.00610	524	1.57
0.254	5.680	0.01705	629	1.89
0.382	8.990	0.0270	662	1.99
0.058	0.815	0.00245	395	1.185
0.086	1.384	0.00416	451	1.356
0.129	2.288	0.00687	498	1.495
0.177	3.440	0.01033	546	1.64
0.209	4.210	0.01263	566.5	1.70

(Ebullioscopic constant taken as 28.14, from calibration with benzil as solute.)

*Solubility Measurements.*

These were made by the usual analytical method, the two phases being stirred together for various periods, after which the solutions were withdrawn, filtered, and analysed. All outlets were protected

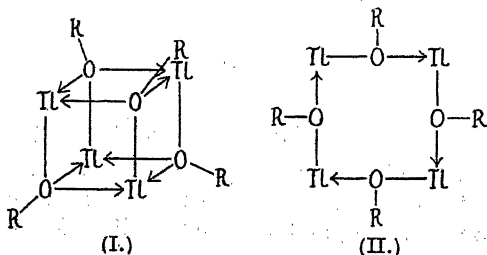
with sulphuric acid tubes, and a mercury-sealed stirrer was used, in order to prevent the ingress of moisture.

The observed solubilities at 25° were : thallous ethoxide in ethyl alcohol, 9.108 g. /100 g.; thallous methoxide in methyl alcohol, 1.703 g./100 g.; thallous methoxide in benzene, 3.16 g./100 g.

These are the mean values of sets of readings which each included one result obtained by saturating for at least 11 hours.

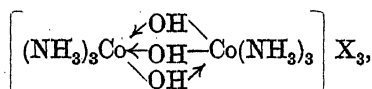
### *Discussion of Results.*

Both the aliphatic and the aromatic alcoholates of thallium behave in water as salts, and their differences in such properties as ease of hydrolysis can be explained by the differing acidities of the parent alcohols. They all dissolve in benzene, however, as much as covalent compounds could be expected to do, which shows that they are covalent in benzene and therefore, presumably, in the solid state. In these solutions they are highly associated, fourfold association being already complete when the *actual* concentrations (of the polymeride) are only about  $N/20$  in the case of the four aliphatic compounds examined and the *o*- and *m*-methoxyphenoxides. The phenoxide and the *o*-vanillin derivative, at actual concentrations of  $N/100$ — $N/50$ , are already associated about three times, but their sparing solubility prevents measurements at higher concentrations. The ethoxide (but not the benzyloxide) appears to undergo a slow further polymerisation in more concentrated solutions. Its complex is, moreover, stable in ethyl alcohol, but the methoxide is apparently unimolecular in methyl alcohol. Though both of these are more soluble in benzene than in their parent alcohols, the difference (at 25°) is less for the methoxide (benzene, 3.16 g./100 g.; methyl alcohol, 1.7 g./100 g.) than for the ethoxide (completely miscible with benzene; ethyl alcohol, 9.1 g./100 g.), which is probably connected with the difference of molecular states in the alcohols. From this it is evident that a fourfold polymeride exists which has a very considerable degree of stability and must, therefore, have a structure which explains why the alcoholates associate readily up to four times, and no further. One possibility is a cubic structure (I) and another is an eight-membered ring structure (II) :—



In the former structure the thallium, having gained one electron from the normal covalency and two from each co-ordinate link, has a complete octet 2, 3, 3, this including the two electrons which are inert in the normal thallos compounds. The oxygen atoms have each formed two co-ordinate links and so have completely shared octets as in basic beryllium acetate (Morgan and Bragg, *Proc. Roy. Soc.*, 1923, 104, 437; Sidgwick, *Nature*, 1923, 111, 808). The further polymerisation could be accounted for by assuming the formation of a co-ordinate link from a thallium atom in one molecule to one in another. In the ring structure each thallium atom has four shared electrons, having gained one by forming a covalency and two from the donor link, so it would probably have a shared quartet outside the core plus the "inert pair" (78) (2), 2, 2. Each oxygen has two ordinary covalencies and one co-ordinate link, as in the majority of its co-ordination compounds. Further polymerisation could occur either by the formation of a double bond between one or more pairs of thallium atoms in different molecules, or by the formation of a co-ordinate link from oxygen to thallium.

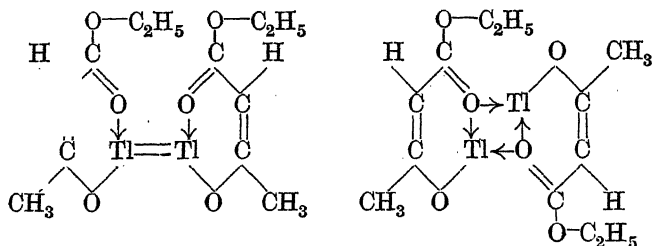
The main difficulty in the cubic structure is that it would certainly be highly strained, though a compound,



the existence of which was established by Werner (*Ber.*, 1907, 46, 4834), would have approximately the same degree of strain per atom, if the metallic atoms in each be assumed to have their valencies normally at right angles, as is certainly the case for the cobalt and possibly for the thallium. If not, the strain would be about twice as great as in this other compound. There is, on the other hand, a strong *a priori* objection to the ring structure inasmuch as no eight-membered chelate rings, in the strict sense of the word, are definitely known to exist (Sidgwick, "Electronic Theory of Valency," p. 251), whereas six-membered chelate rings are very common, and, therefore, if a ring compound were to be formed by polymerisation, we should expect it to be a three-fold and not a four-fold complex. In both formulæ we postulated that the thallium should accept co-ordinate links, but it is remarkable that it does not appear to do this from pyridine or acetone; the thallos phenoxides can be precipitated unchanged from pyridine solutions by ligroin, or recrystallised from acetone. Moreover, the one type of thallos ammine reported (Biltz and Stollenwerk, *Z. anorg. Chem.*, 1921, 119, 97) is only formed in liquid ammonia.

Ethyl thalloacetoacetate was found not to be a simple co-ordin-

ation compound, but to be completely polymerised to a two-molecular complex in a solution  $N/8$  in *actual* concentration. This polymeride could be formed in either of two ways. First, by the formation of a double bond between the two thallium atoms, which was suggested as a way in which the eight-membered ring might polymerise; this would be analogous to the readiness of the inert pair of electrons to partake in the formation of a completely shared octet, which is so marked in lead.



Secondly, co-ordinate links from oxygen to thallium could be formed, so that the thallium would be given a mixed octet, as in the suggested cubic structure. In fact, the whole similarity of the two structures may be taken to support both. Thallous acetylacetonate was reported by Kurowski (*Ber.*, 1910, **43**, 1078) to be unimolecular in ethyl alcohol, but we could not confirm this; we obtained irregular results suggestive, possibly, of alcoholysis. We should expect the thallous derivative of *o*-vanillin to behave in the same way, but actually, as previously stated, it appears to be associated largely to the four-fold polymeride.

These results are of interest in their bearing on Sugden's deductions from the parachors of thallium compounds (*J.*, 1929, 316). He there claims to have shown that the parachor of thallium in ethyl thalloacetoacetate is approximately the same as in dimethylthalliumbenzoylacetone, whether we assume singlet or duplet linkages, and the same as in thallous ethoxide, formate, and acetate, if we assume singlet linkages in the first two, and duplet linkages in the last three substances. If we assume that no allowance has to be made for the tervalency of the oxygen, the eight-membered ring structure gives parachor values for thallium practically identical with those derived from the unimolecular formula, on either the singlet or the duplet link hypothesis (*ca.* 62 for duplet links, and 85 for singlet links). The cubic structure involves parachors for thallium of about 48 for duplet links and less than 30 for singlet links. In order to derive a parachor value of about 62 from ethyl thalloacetoacetate, which we now know to be bimolecular, we must assume that all the thallium linkages (including those uniting the two

simple molecules) are singlet links; all other assumptions give lower values. Thus, the difficulty of reconciling the various data for  $P_m$  is that we have to assume that the polymerisation arises from the formation of duplet links in the case of the ethoxide and singlet links in the case of the acetoacetic ester derivative.

We should expect that, if the cubic structure were the correct one, crystals of the alcoholates would be cubic. From the previously mentioned crystallographic examination of the benzyloxide (the only derivative which gave suitably large crystals) this obviously was not so, but the cubic structure is not definitely ruled out as a consequence; carbon tetrabromide is cubic above  $46.68^\circ$ , but monoclinic below this temperature (Zirngiebl; compare Groth, "Chemische Krystallographie," Vol. I; [Leipzig, 1906], p. 229).

Though the structure of the four-molecular complex cannot be settled from the available evidence, its stable existence is interesting, since it shows that mono-covalent thallium, which could have a partially shared quartet (78), 2, 1, 1, or a shared pair outside the core plus the inert pair (78) (2), 1, 1 (compare the mercurous ion), although it can exist, is very unstable, and this may be correlated with the fact that no monoalkyl derivative of thallium has yet been isolated.

We should like to express our thanks to Dr. R. C. Menzies for his great kindness in supplying specimens of several thalloses compounds and for his helpful advice regarding the preparations; also to Imperial Chemical Industries Ltd. for a grant towards the expenses of the research.

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[Received, May 13th, 1930.]

## CLXXXIX.—*The Polysulphides of the Alkali Metals.* *Part I. Sodium (i).*

By THOMAS GIBSON PEARSON and PERCY LUCOCK  
ROBINSON.

IN spite of much research, little is definitely known of the polysulphides of the alkali metals, for none of the earlier work has escaped criticism, and, indeed, only the latest work, that of Rule and Thomas (J., 1914, 105, 177, 2819; 1917, 111, 1063), has remained unchallenged. Two anomalies, typical of many, are that one published equilibrium diagram shows *eight* and another *four* compounds; also, that the existence of a series of disodium compounds, described

either by Schöne or by Böttger, was contradicted by Bloxam, whose tetrasodium enneasulphide, in turn, Rule and Thomas were unable to prepare. Moreover, certain standard treatises in English appear to have been misled by several mistranslations in abstracts. In view of the great diversity of opinion, and as we were interested in the individual polysulphides as a possible source of pure persulphides of hydrogen (compare Mills and Robinson, J., 1928, 2326), we decided that an extensive re-examination of this field was essential.

The present paper describes a careful reinvestigation of all the previous work on the polysulphides of sodium, with the exception of that of Hugot (*Compt. rend.*, 1899, **129**, 388) in liquid ammonia, of Küster and Heberlein on the electrochemistry of aqueous polysulphide solutions, and of Sabatier (*Ann. Chim. Phys.*, 1881, **22**, 15) on thermochemical aspects. An endeavour to account for previous discrepancies has in great measure been successful. Moreover, certain other methods of attack have been applied to these problems for the first time, particularly (1) the amplification of thermal analysis of the system sodium monosulphide-sulphur by microscopic methods; (2) the confirmation of the existence of di-, tetra-, and penta-sulphides in melts by measurement of the loss of sulphur at various temperatures; and (3) the partial study of the system sodium monosulphide-sulphur-water-alcohol.

The conclusions reached are summarised on p. 1496. The peculiar stability of sodium tetrasulphide is significant. It appears to be readily obtained from solution in both anhydrous and hydrated forms and, furthermore, to be the only polysulphide obtainable from the hydrosulphide. Trisulphide, on the other hand, appears to be formed at 120° but to be completely decomposed into a mixture of di- and tetra-sulphides at temperatures far below its melting point. It would seem, however, that this stability is an inherent property of the molecular type  $\text{Na}_2\text{X}_4$ , rather than of the tetrasulphide itself, since dehydration of the highest hydrates at 100° produces  $\text{Na}_2\text{S}_3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{S}_2\cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{S}_3\cdot \text{H}_2\text{O}$ , and  $\text{Na}_2\text{S}_4$ , and leads to the hydrolysis of pentasulphide.

Further work, designed to elucidate the structure of these polysulphides, is in progress.

#### EXPERIMENTAL.

*Preparation of Materials Used.*—The sodium from Imperial Chemical Industries, Ltd., was kept under dry liquid paraffin containing 1% of amyl alcohol, which is known to preserve a fresh metallic surface. Experience enabled the metal to be cut to within 0.1 g. of the desired weight, thereby reducing oxidation to a minimum.



The sulphur was twice recrystallised from carbon disulphide and dried for several hours at  $100^{\circ}$ .

Absolute alcohol was dried by being twice refluxed for 3 hours over freshly burnt quick-lime and then distilled from the same material, with rejection of small head and tail fractions.

Toluene was dried by refluxing over metallic sodium, then over a polysulphide, and distillation from metallic sodium, small head and tail fractions being rejected.

*Analytical Methods.*—The total sulphur content was determined by adding a weighed amount of the polysulphide in aqueous solution to 50 c.c. of 10% sodium hydroxide containing 7 c.c. of bromine. The solution was gently heated until of a light straw colour, whereupon 30 c.c. of hydrochloric acid were added and the whole was boiled until colourless. The sulphate was then estimated in the usual way with barium chloride.

The polysulphide sulphur and the sodium were determined together on the same weighed sample: (1) a slight excess of 10% sulphuric acid was added, and the solution boiled to coagulate the precipitated sulphur, which was filtered, thoroughly washed, and dried in an electric oven at  $70-80^{\circ}$ ; (2) the filtrate was concentrated to a suitable volume, transferred to a platinum dish, evaporated to dryness, fused to the sulphate, and weighed.

Blanks were done on all the reagents used.

Experimental details are described under the relevant sections.

### I. The Preparation of Polysulphides from Solution.

(i) *The Action of Sulphur on Sodium Monosulphide in Aqueous Alcohol.*—Schöne (*Pogg. Ann.*, 1867, **131**, 380) dissolved excess of sulphur in aqueous sodium monosulphide, evaporated the solution to crystallisation in a vacuum, triturated it with alcohol, and cooled it in a freezing mixture, obtaining pale yellow plates of hydrated sodium tetrasulphide,  $\text{Na}_2\text{S}_4 \cdot 6\text{H}_2\text{O}$ . The mother-liquor on being chilled after further concentration gave orange-yellow crystalline pentasulphide,  $\text{Na}_2\text{S}_5 \cdot 6\text{H}_2\text{O}$ . Later, Filhol (*Ann. Chim. Phys.*, 1873, **28**, 529) failed to obtain any polysulphides from sulphur and aqueous monosulphide in sealed tubes, but Böttger (*Annalen*, 1884, **226**, 335) described the formation of four polysulphides,  $\text{Na}_2\text{S}_2 \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{S}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{S}_4 \cdot 8\text{H}_2\text{O}$ , and  $\text{Na}_2\text{S}_5 \cdot 8\text{H}_2\text{O}$ , by solution of the calculated amounts of sulphur in aqueous-alcoholic sodium monosulphide. These results were criticised by Bloxam (*J.*, 1900, **77**, 753) on the grounds that the alleged polysulphides could not have been formed since the sulphur added did not allow for the simultaneously formed thiosulphate (compare *Chem. News*, 1895, **72**, 63), or, alternatively, if formed, the polysulphides would have

been contaminated with this thiosulphate, which becomes soluble in alcohol in their presence; further, he criticised the absence of data as to yield or description of the product, and doubted whether any pure polysulphide had been obtained. In consequence, Bloxam attempted to prepare them by the action of sulphur on aqueous hydrosulphide in a stream of hydrogen sulphide, but obtained only an alleged tetrasodium enneasulphide,  $\text{Na}_4\text{S}_9 \cdot 14\text{H}_2\text{O}$  (compare p. 1483).

Küster and Heberlein (*Z. anorg. Chem.*, 1905, **43**, 53, 431) found that the solubility of sulphur in solutions of the monosulphide diminished only slightly with rise in temperature between  $0^\circ$  and  $50^\circ$  and depended mainly on the concentration of the monosulphide, being at a maximum at  $0.063N$ ; the elements were then present in the atomic ratio  $\text{Na} : \text{S} = 2 : 5.24$ . They advanced evidence that a complex equilibrium rather than definite compounds existed in the solutions. They also noted the unique stability of solutions of tetrasulphide composition and showed that the polysulphides undergo hydrolysis to an extent which diminishes regularly with increasing sulphur content.

It is evident that the formation of a number of polysulphides by Böttger's method was possible, and that the problem could be best solved by a phase-rule study of the system monosulphide-sulphur-water-alcohol. As a complete investigation was impracticable, however, we examined the solid phases separating from a series of solutions having a wide range of  $\text{S} : \text{Na}$  ratios at one temperature, viz.,  $-18^\circ \pm 2^\circ$  (compare Lash Miller and Kenrick, *J. Physical Chem.*, 1903, **7**, 259). These ratios for corresponding solid and liquid phases are plotted in Figs. 1a and 1b, and indicate unquestionably the formation of hydrated forms of di-, tri-, tetra-, and penta-sulphide, excluding the possibility of solid solutions. The work of Böttger and Schöne is therefore confirmed, although in several cases our hydrates differed from theirs; the new hydrates are:  $\text{Na}_2\text{S}_2 \cdot 6\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_3 \cdot 8\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_4 \cdot 9\text{H}_2\text{O}$ ; and  $\text{Na}_2\text{S}_4 \cdot 11\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_5 \cdot 6\text{H}_2\text{O}$ . To these must be added a tetrasulphide which may be either a hepta- or a mixture of octa- and hexa-hydrates. Dehydration of these materials at  $100^\circ$  led to the formation of  $\text{Na}_2\text{S}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{S}_3 \cdot \text{H}_2\text{O}$ . A more extensive study of these hydrates is being undertaken by means of vapour-pressure measurements.

We therefore dissent from Bloxam (*loc. cit.*), not only as to the formation of these compounds, but also as to their alleged serious contamination with thiosulphate and alcohol: with suitable precautions only traces of these substances are present. Further, it is significant that Biltz and Wilke-Dörfurt (*Ber.*, 1905, **38**, 123; *Z. anorg. Chem.*, 1906, **48**, 297) prepared rubidium and caesium poly-

sulphides by a similar method without observing the formation of thiosulphates.

FIG. 1a.

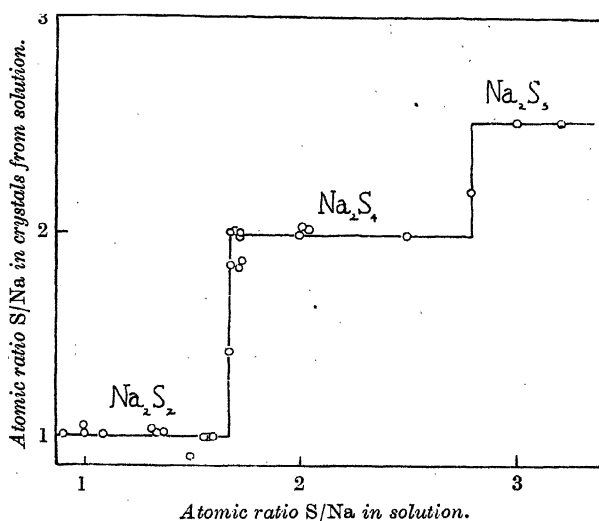
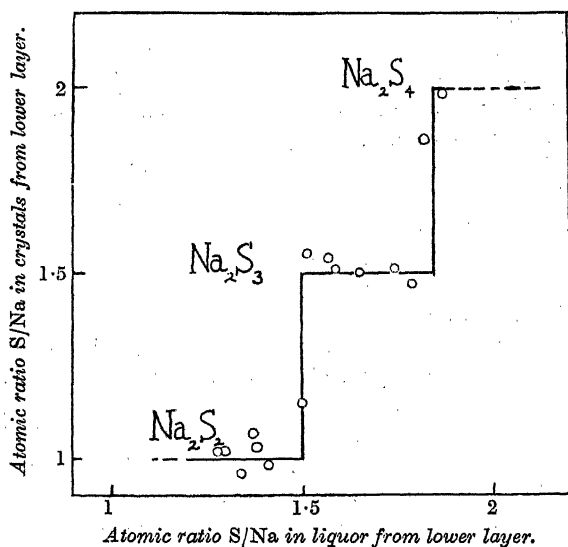


FIG. 1b.



*Experimental.* Solutions of the hydroxide for conversion to monosulphide were prepared by the action of clean metallic sodium on aqueous alcohol (Küster, *Z. anorg. Chem.*, 1904, **41**, 474) of

known composition. One-half of the solution was treated with hydrogen sulphide, giving pearly crystals which redissolved as saturation proceeded. The addition of the second half of the caustic soda immediately produced a nacreous crystalline precipitate which disappeared on warming. In this solution the requisite weight of sulphur was then dissolved by gentle heating on the water-bath for the minimum time. The resulting solutions varied in colour from light yellow at the disulphide composition to deep red at the pentasulphide. Within a specific range of composition, between di- and tetra-sulphide, a dark-coloured oil separated as a lower layer from the bulk of the solution on standing (see below).

The solutions—separated from the oils where necessary—were sampled for analysis and then crystallised in standard freezing mixtures of salt and ice (*i.e.*, at  $-18^{\circ} \pm 2^{\circ}$ ) except in runs 27 and 28, in which cooling was effected in ether and solid carbon dioxide at about  $-60^{\circ}$ . In the preliminary experiments, the solutions were crystallised completely in one cooling period of several hours, but the products generally had complex S : Na ratios and, as shown by subsequent fractional crystallisation, were mixtures formed by the successive crystallisation of individual polysulphides. In those exceptional cases, however, where large fractions of definite stoicheiometric composition were obtained, the first solid phase had obviously continued to be formed although metastable to the changed liquid, *e.g.*, runs 15, 16, 17. In general, therefore, fractions of crystals small enough to effect but little alteration in the composition of the solution were removed by filtration, washed first with ice-cold absolute alcohol and then with dry ether, exposed to phosphoric oxide and paraffin chips in a vacuum desiccator for 20 minutes, and analysed. Where large fractions were taken the resultant liquors were analysed (see footnote to runs 5, 15, 16, 17, 19, Table I). The results are shown in Table I and Fig. 1*a*, the S/Na ratios being, as elsewhere, atomic ratios. The "polysulphide" sulphur is denoted throughout by (S).

The red oily liquid separating when the ratio S : Na in the solution was between 1.09 and 1.94 proved to be an aqueous polysulphide of such high concentration as to suggest that it consisted of molten hydrates; moreover, it invariably approximated to the trisulphide in composition, *e.g.*, when the upper layer had S : Na = 1.879 : 1, the lower had the ratio 1.650 : 1. The oils were sampled for analysis, cooled to  $-7^{\circ}$ , and the smallest possible fraction of crystals was separated and dried as above. This was extremely difficult, for, once started, crystallisation tended to spread rapidly through the system. The mother-liquors after filtration were therefore frequently analysed to check changes due to the crystallisation

TABLE I.

No.	Solution.				Crystals.			
	Na, g.	Water, c.c.	Alcohol, c.c.	S/Na.	Na, %.	(S), %.	S, %.	S/Na.
1	6	65	25	0.974	20.33	13.83	28.94	1.023
2	6	65	25	1.007	20.33	14.20	30.00	1.061
3	6	80	6	1.007	21.68	14.53	30.10	1.021
4	6	80	6	1.007	24.36	17.39	35.00	1.033
†5	6	80	25	1.087	21.25	13.83	29.50	1.021
6	6	80	12	1.322	20.51	17.10	29.75	1.042
7	6	85	25	1.348	19.63	13.26	27.27	1.033
8	6	65	25	1.383	20.56	16.63	29.36	1.027
9	3.7	80	7.5	1.503	21.20	14.31	28.62	0.970
10	6	80	10	1.561	21.11	14.75	29.62	1.009
11	6	6	25	1.564	21.09	—	29.92	1.016
12	5.6	84	6	1.618	21.23	13.37	29.37	0.994
13	6	80	7.5	1.602	21.22	13.55	33.53	1.136
14	6	65	25	1.685	16.10	20.33	—	1.408
†15	6	80	25	1.689	16.44	31.17	42.67	1.839
†16	6	85	20	1.680	16.02	32.24	44.16	1.982
†17	6	65	25	1.706	19.58	38.97	53.65	1.970
18	6	80	10	1.718	15.85	24.77	39.41	1.787
†19	6	80	25	1.744	16.02	30.82	41.24	1.854
20	6	65	25	1.744*	15.75	31.65	43.12	1.967
21	6	65	25	1.744*	15.76	31.58	42.90	1.957
22	6	65	25	1.744*	15.72	31.54	43.31	1.980
23	6	80	12	1.946	15.73	36.08	46.22	2.112
24	6	65	25	1.999	14.75	29.51	42.43	2.068
25	6	65	35	1.999*	14.14	29.73	39.14	1.989
26	6	65	25	1.999*	15.43	31.32	43.36	2.020
27	6	65	40	1.999*	13.59	28.75	38.06	2.013
28	6	65	40	1.999*	12.49	25.64	34.10	1.962
29	6	70	25	2.500	15.61	32.01	42.92	1.976
30	4	60	15	2.814	15.33	37.59	48.25	2.262
31	6	65	15	3.011	14.70	40.45	51.15	2.502
32	6	65	15	3.219	14.68	40.62	51.20	2.506

\* Computed from weight of sulphur added, not by analysis of solution.

† The S/Na ratio in solution after crystallisation in these runs was as follows :

Run .....	5	15	16	17	19
Ratio .....	1.216	1.228	1.144	1.276	1.721

of too large a fraction. The results are given in Table II and Fig. 1b.

The products were tested for the presence of alcohol by distilling 5 g. samples in nitrogen until all volatile matter had been evolved, the water condenser finally being thoroughly rinsed into the ice-cooled receiver. The distillate was then submitted to Dupré's modification of Thresh's test [*Pharm. J.*, (3), 9, 408], and the quantity of alcohol shown to be less than 0.02% of the original crystals. Comparative experiments using the iodoform reaction indicated a quantity of the order of 0.01%. Thiosulphate, produced partly by aerial oxidation and partly by solution of sulphur in the hydrolysed monosulphide, was invariably present in small quantities in the crystals; that due to oxidation could be minimised by

TABLE II.

Oil.					In solution.			
No.	Na, g.	H <sub>2</sub> O, c.c.	Alcohol, c.c.	S/Na.	Na, %.	(S), %.	S, %.	S/Na.
*33	6	80	25	1.279	21.40	14.33	30.29	1.018
34	6	85	25	1.292	21.08	14.15	29.85	1.018
35	6	80	25	1.344	22.05	13.80	29.57	0.964
36	6	80	25	1.374	20.03	14.77	29.99	1.076
37	6	85	25	1.383	20.55	16.00	29.40	1.029
*38	6	80	25	1.409	22.13	15.05	30.28	0.983
39	6	80	25	1.499	21.97	19.00	35.21	1.152
40	6	65	25	1.512	16.19	23.88	34.95	1.548
*41	6	60	25	1.574	16.25	22.55	34.73	1.536
42	6	80	25	1.585	16.35	23.20	34.42	1.514
*43	5.15	60	25	1.650	16.11	22.76	33.74	1.501
44	6	60	35	1.743	16.02	22.56	33.72	1.513
45	6	80	25	1.790	17.45	23.34	35.85	1.477
*46	6	80	25	1.826	16.51	32.25	42.85	1.864
47	6	65	25	1.870	15.85	31.32	43.85	1.988

\* The S/Na ratio in solution after crystallisation in these runs was :

Run .....	33	38	41	43	46
Ratio .....	1.512	1.790	1.620	1.790	1.905

avoiding access of air to the polysulphides or their solutions, and the remainder by dissolving the sulphur as quickly as possible in the monosulphide at the lowest convenient temperature, *viz.*, 60°. If the first precaution was not observed, 20 minutes' boiling gave in octahydrated tetrasulphide crystals a thiosulphate content of 2.6—3.0%; by careful exclusion of air, this was reduced to 1.6%, and the second precaution reduced this still further to 0.5—1%.

*Properties of the hydrated polysulphides.* The disulphide *hexahydrate* is a cream-coloured, acicularly crystalline compound; like the other hydrated sulphides, it is very soluble in water and less so in alcohol, giving clear, light yellow solutions. The mean of the analyses of twelve different samples gave: Na,  $21.11 \pm 0.23$ ; (S),  $14.51 \pm 0.33$ ; S,  $29.79 \pm 0.23$  [ $\text{Na}_2\text{S}_2 \cdot 6\text{H}_2\text{O}$  requires Na, 21.10; (S), 14.68; S, 29.36%]. Two samples when heated at 100° in a stream of pure hydrogen lost 34.20 and 34.80% of water, giving the *dihydrate* ( $\text{Na}_2\text{S}_2 \cdot 6\text{H}_2\text{O}$  requires  $4\text{H}_2\text{O}$ , 33.02%). The hexahydrate on heating to 200° could be almost completely dehydrated (Loss: 47.80, 48.50, 48.82. Calc.: 49.54%), but the removal of the last trace of water involved loss of hydrogen sulphide.

The hydrated trisulphide obtained from the oily layer consisted of dark yellow lamellæ melting at about 25° to a thick, oily, reddish-brown liquid. It appeared to be an *octahydrate* [Found (mean of 17 analyses on independent preparations): Na,  $16.21 \pm 0.14$ ; (S),  $23.08 \pm 0.40$ ; S,  $34.03 \pm 0.20$ .  $\text{Na}_2\text{S}_3 \cdot 8\text{H}_2\text{O}$  requires Na, 16.08; (S), 22.38; S, 33.57%]. On dehydration at 100° in a stream of hydrogen, three samples lost 43.96, 44.92, and 44.49% of water,

giving a *monohydrate* ( $\text{Na}_2\text{S}_3 \cdot 8\text{H}_2\text{O}$  requires  $7\text{H}_2\text{O}$ , 44.05%). The remaining water cannot be completely removed without considerable hydrolysis; e.g., at  $200^\circ$  three samples lost 47.94, 48.51, 49.20% (Calc. for  $8\text{H}_2\text{O}$  : 50.35%).

The hydrated tetrasulphides formed golden-yellow, glistening plates. The degree of hydration depended upon temperature and water concentration of the liquid from which they were crystallised. With high water content at low temperatures, two higher *hydrates* were obtained [Found in *A* : Na, 13.59; (S), 28.75; S, 38.05.  $\text{Na}_2\text{S}_4 \cdot 9\text{H}_2\text{O}$  requires Na, 13.69; (S), 28.58; S, 38.10%. Found in *B* : Na, 12.49; (S), 25.64; S, 34.10.  $\text{Na}_2\text{S}_4 \cdot 11\text{H}_2\text{O}$  requires Na, 12.37; (S), 25.81; S, 34.41%]. When the water content was reduced, an octahydrate separated [Found (mean of 8 analyses on 8 different samples) : Na,  $14.45 \pm 0.14$ ; (S),  $29.62 \pm 0.40$ ; S,  $40.78 \pm 0.32$ . Calc. : Na, 14.47; (S), 30.19; S, 40.26%]. By reducing the proportion of water or raising the temperature, a product which might be either a hepta- or mixture of hexa- and octa-hydrates was obtained [Found : Na, 15.76; (S), 31.58; S, 43.24. Calc. for heptahydrate : Na, 15.33; (S), 32.00; S, 42.66%].

Dehydration of any of these preparations at  $100^\circ$  gave no evidence of lower hydrates, and the whole of the water could be removed at  $140^\circ$  : thus three separate samples of octahydrate lost 46.35, 44.92, and 45.67% (Calc. : 45.27%).

The pentasulphide is an orange-coloured hexahydrate, crystallising in minute plates [Found : Na, 14.67; (S), 40.54; S, 51.18. Calc. : Na, 14.65; (S), 40.77; S, 50.96%]. This material obviously suffered decomposition by hydrolysis on dehydration even at  $100^\circ$ .

(ii) *The Action of Sulphur on Anhydrous Alcoholic Solutions of Sodium Monosulphide*.—Solutions of polysulphides have been prepared by dissolving sulphur in alcoholic solutions of sodium monosulphide. Through an examination of the solids crystallising from solutions varying considerably in the ratio S:Na, it has been established that, although unsuitable for preparation of pure polysulphides, the method yields di-, tri-, tetra-, and probably penta-sulphide. There is also some evidence of the existence of alcoholates, and this is being investigated by means of vapour-pressure measurements.

*Experimental*. A solution of sodium (4 g.) in anhydrous alcohol was converted to the monosulphide by dividing it into two equal portions, saturating one with hydrogen sulphide, gently boiling it in a stream of nitrogen to remove excess of gas, and adding it to the other. The requisite weight of sulphur was dissolved by boiling for the minimum time. The resulting liquids were, after analysis, partly crystallised by evaporation in a vacuum at  $15^\circ$ .

The small fraction of crystals deposited was quickly collected on a Buchner funnel, well pressed, washed with several small quantities of anhydrous alcohol, dried by exposure to calcium chloride in a vacuum desiccator, and analysed. The results are in Table III.

The solubility of the polysulphides increased with their sulphur content, so that with solutions above the tetrasulphide composition the separation of a primary fraction was prevented by crystallisation taking place in one stage with the removal of all but the last trace of alcohol. These products obviously had the composition of the mother-liquor and were therefore examined under the microscope without analysis. About the composition  $\text{Na}_2\text{S}_{4.5}$ , a large proportion of yellow crystals, typical of tetrasulphide, appeared, together with some brownish-yellow crystals, characteristic of pentasulphide. The light yellow constituent was largely replaced by the darker constituent at about the pentasulphide stage, whilst in the hexasulphide region this replacement was complete, but light yellow crystals of sulphur appeared. The products were in every case homogeneous microcrystalline polysulphides, uncontaminated by thiosulphate, but containing alcohol in such quantities as to indicate the presence of alcoholates (compare Rule and Thomas, J., 1914, 105, 177). The disulphide was golden-yellow, acicular, and microcrystalline; the trisulphide formed dull yellow, tabular crystals; the tetrasulphide, dull yellow cubes with an olive-green tinge; and the pentasulphide, deep, orange, tabular crystals.

TABLE III.

Solution.	Crystals.					Solution.	Crystals.				
	% (S).	% S.	% S.	S/Na.	S/Na.		% (S).	% S.	% S.	S/Na.	S/Na.
1.100	40.73	27.69	56.41	0.996	1.675	25.46	45.01	62.80	1.773		
1.250	25.88	37.31	52.91	1.471	1.751	22.04	45.63	61.14	1.994		
1.501	27.41	38.15	57.36	1.505	2.001	26.41	54.00	72.00	1.960		
1.600	27.11	37.36	56.22	1.490	2.150	25.33	53.22	71.87	2.040		

(iii) *The Action of Sulphur on Sodium Hydrosulphide.*—Rule and Thomas (*ibid.*) dissolved various proportions of sulphur in a solution of sodium hydrosulphide in anhydrous alcohol and found pure tetrasulphide to be formed only with the elements present in the calculated ratio. With less sulphur the products were considered to be mixtures of tetrasulphide and unchanged hydrosulphide, with pentasulphide proportions a mixture of tetrasulphide and sulphur resulted, but with more sulphur still there was some indication of higher polysulphides in the mixture. These authors confirmed their conclusions by estimating the hydrogen sulphide evolved during the dissolution of the sulphur.

We have repeated and confirmed these results, and have extended



the experiments to aqueous-alcoholic solutions. This was done because the nearly equal solubility of hydrosulphide and tetrasulphide in anhydrous alcohol makes it impossible fractionally to separate them from this medium. In aqueous alcohol, however, the former appears to be definitely less soluble than the latter, and thus it has been possible to crystallise tetrasulphide as a late fraction even from solutions initially containing only sufficient sulphur to form trisulphide. Consequently, it would seem that sodium tetrasulphide is the only product from hydrosulphide over an extended range of sulphur concentration.

Bloxam (*loc. cit.*) stated that only one definite compound, *viz.*,  $\text{Na}_4\text{S}_9 \cdot 14\text{H}_2\text{O}$ , could be obtained from solutions of sulphur in aqueous hydrosulphide. In an endeavour to obtain such tetrasodium salts, we passed hydrogen sulphide through aqueous-alcoholic solutions of the hydrosulphide whilst the sulphur was dissolving. Products of extremely variable composition were obtained, and only a fortuitous choice would have given compounds apparently of the type described by Bloxam. If such compounds were actually produced, they would have to contain at least 14 molecules of water. This high state of hydration is unusual, and the cumulative evidence suggests that the materials were *mixtures* of disodium compounds.

*Experimental.* 6-G. portions of sodium, dissolved in 150-c.c. lots of pure dry alcohol, were converted to hydrosulphide by the usual process (p. 1478); in the gently boiling solutions the required weights of sulphur were dissolved, and the solutions were evaporated to crystallisation or precipitated with dry ether. In appearance, composition, and properties, the products so obtained were identical with those described by Rule and Thomas (*loc. cit.*, pp. 179—183), tetrasulphide being the only definite polysulphide. The formation of disulphide by the action of sodium on the tetrasulphide was also confirmed (*idem, ibid.*, pp. 187—188), and, by a modification of these authors' method, we obtained further support for our results by measuring the hydrogen sulphide evolved during the dissolution of the sulphur.

For work in aqueous alcohol, lots of 10.3 g. of sodium were converted to hydrosulphide in an alcohol-water mixture (120 and 65 c.c. respectively), and sufficient sulphur was subsequently added to give the trisulphide composition. In the first case, the solution, after being kept at  $-22^\circ$  for 7 hours, deposited a large mass of plate-like crystals [Found: Na, 15.51; (S), 26.59; S, 36.75%; Na:S = 1:1.703]. In a second preparation, the material was fractionally crystallised; the first fraction, produced by cooling to  $-15^\circ$  for one hour, was presumably a mixture of tetra- and hydro-sulphides

[Found: Na, 15.44; S, 41.82%; Na:S = 1:1.947], whilst a second fraction, obtained by cooling to  $-22^{\circ}$  for 2 hours, and a third, by evaporating the mother-liquor to half bulk in a vacuum at room temperature followed by cooling to  $-30^{\circ}$ , were pure tetrasulphide [Found: for (ii), Na, 15.62; S, 43.64; for (iii), Na, 14.68; S, 41.00%; Na:S = 1:2.009, 1:2.007].

These experiments were modified by passing hydrogen sulphide through the liquid during the dissolution of the sulphur, but the solids produced on cooling were of indefinite and variable composition.

## II. *Preparation of Polysulphides by Dry Methods.*

(i) *Reaction between Sulphur and Sodium Carbonate or Hydroxide.*—Polysulphides have been prepared by the action of sulphur on heated metallic oxides, hydroxides, or carbonates. Berthollet (*Ann. Chim.*, 1798, 25, 233) believed them to be pure, and ascribed the occurrence of sulphate in their solutions to a reaction with water, but Gay-Lussac (*ibid.*, 1811, 78, 87) and Vauquelin (*Ann. Chim. Phys.*, 1817, 6, 5) contended that it was a primary product, and this was confirmed by numerous subsequent workers. Fordos and Gelis (*Ann. Chim. Phys.*, 1846, 18, 86) found that a similar reaction took place in solution, producing thiosulphate and polysulphide, and Rose (*Annalen*, 1829, 17, 324; 1842, 45, 415, 533) confirmed this for potassium carbonate.

These results assume importance through Friederich's claim (*Met. Erz.*, 1914, 11, 80) to have obtained pure polysulphides by the reaction between sulphur and sodium carbonate in carbon dioxide, and through his having used them in the investigation of the sodium sulphide-sulphur equilibrium (see p. 1489).

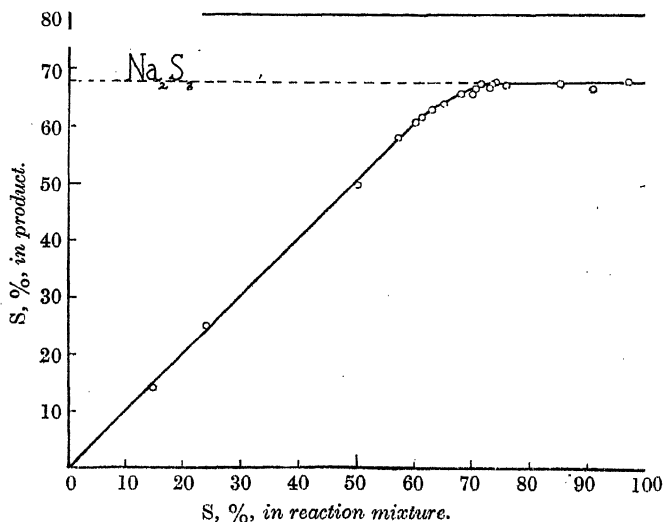
*Experimental.* 8.21 G. of sulphur and 6.79 g. of anhydrous sodium carbonate were heated under nitrogen. Reaction commenced slowly at about  $200^{\circ}$ , giving thiosulphate and polysulphide. At  $350^{\circ}$  the product contained 11.25% of thiosulphate, less than 0.05% of sulphate, and some unchanged material; whilst at  $640^{\circ}$  a loss of 2.85 g., corresponding to the whole of the carbon dioxide in the carbonate, was found, and the residue contained 17.70% of sodium sulphate and 4.22% of sodium sulphite, but no thiosulphate.

Analogous reactions were observed with sodium hydroxide, but similar experiments in boiling aqueous solutions led only to thiosulphate and polysulphide.

(ii) *The Action of Sodium on Sulphur.*—The preparation of polysulphides by the action of metallic sodium on molten sulphur has been attempted by Jones (J., 1880, 37, 1461), Rosenfeld (*Ber.*, 1891, 24, 1658), and others. The method is unsatisfactory owing to the

violence of the combination and to contamination of the product either by silicates from the container or by oxidation. A more convenient process, due to Locke and Austell (*Amer. J. Sci.*, 1898, 20, 592), is to allow the elements to react under toluene. From purely qualitative observations of the presence of free sulphur in the toluene or of metallic sodium in the product according as the added sulphur sufficed for the formation of trisulphide or not, these authors concluded that no material is obtainable with less sulphur than a mixture of tri- with some tetra-sulphide. As these results have been generally held by subsequent writers to indicate that only trisulphide is produced under these conditions, we have

FIG. 2.



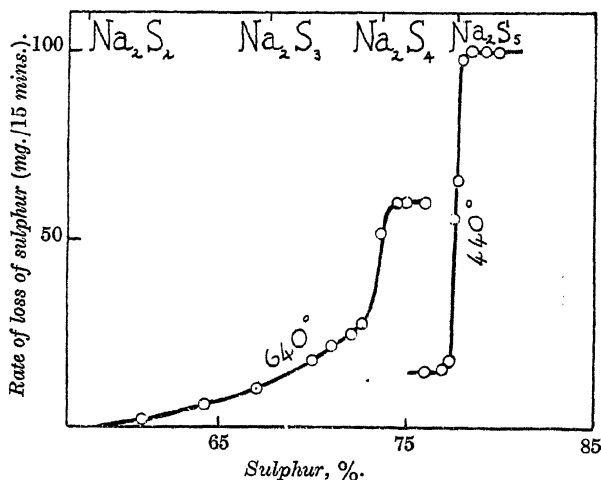
repeated this work quantitatively. Our findings (see Fig. 2) indicate that no compound higher than the trisulphide is produced. Free sodium in diminishing quantities is invariably present until this composition is reached, but not afterwards, provided that the reactants have been brought into intimate contact by crushing. The reaction is unique in that a polysulphide appears to be the first product, for even with a trace of sulphur no white film appears on the sodium surface such as might indicate monosulphide—under these conditions the metallic surface is partially coated with distinctly yellow patches, as though a polysulphide must be formed even at the cost of leaving available surface unattacked.

*Experimental.* The required weight of clean metallic sodium was melted under 250 c.c. of carefully dried toluene in a 500-c.c. flask

fitted with a reflux condenser through which was added a weighed quantity of sulphur in 0.5 g. portions. The sodium was immediately coated with a yellow coherent film, but the reaction did not become vigorous until 1.5 atomic proportions of sulphur had been added, whereupon the film burst. The escaping sodium reacted vigorously with the dissolved sulphur, and it became necessary to cool the flask in water. After each subsequent addition of sulphur, we ground the spongy, friable masses with a long glass pestle to free the imprisoned sodium. Finally, the toluene was boiled for 20 minutes to complete the operation.

The sulphide was quickly collected on a Buchner funnel, well pressed, washed with cold toluene, and heated at  $100^{\circ}$  for 2 hours

FIG. 3.



under a good vacuum applied through a drying train. With material below trisulphide composition, free sulphur was always present at this stage. When, however, sulphur equivalent to pentasulphide was used, there was a tendency for this element to crystallise on the cold filter pad; this was avoided by heating the funnel and washing with boiling toluene. The remainder of the toluene was removed by cautiously melting the sulphide. The products were homogeneous masses of pure sodium sulphides which gave clear solutions in water. If, however, insufficient care was taken to moderate the reaction in toluene by cooling, carbon to the extent of 0.05% might be present. Table IV compares the proportion of sulphur originally used with that found in the final product after melting.

TABLE IV.

S, %, in reactants	14.7	24.2	50.0	57.2	60.0	61.3	63.3	64.7	67.8	69.7
„ in products	14.0	25.0	50.1	58.4	60.9	62.0	63.4	63.8	65.7	66.0
S, %, in reactants	70.6	71.4	73.1	73.7	74.1	74.6	76.2	85.0	91.2	96.8
„ in products	67.2	68.3	66.8	67.8	68.6	68.6	67.6	67.8	67.0	68.1

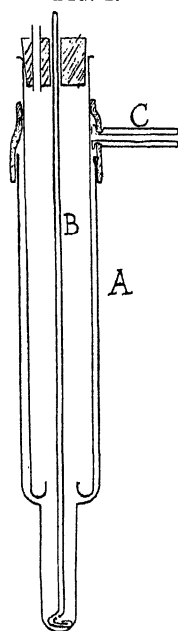
(Calc. for  $\text{Na}_2\text{S}_3$ : S, 67.6%.)

(iii) *Desulphurisation of the Polysulphides*.—Rule and Thomas (J., 1917, 111, 1063) measured the loss in weight of sodium tetrasulphide when heated in a stream of hydrogen for consecutive  $\frac{1}{2}$ -hour periods, the temperature being raised by  $50^\circ$  between each period. The results, when plotted as time against composition, indicated that the disulphide is the most stable polysulphide at high temperatures. Their experiment was not designed to demonstrate the possible existence of lower polysulphides, and indeed, could not have done so, for the period of heating at each temperature was quite insufficient for equilibrium to be reached. In the experiments outlined below, rate of loss of sulphur with changing composition has been determined by weighing the sulphur evolved on heating a known quantity of polysulphide at various fixed temperatures in a stream of nitrogen of constant velocity. The results, shown graphically in Fig. 3, indicate the presence of di-, tetra-, and penta-sulphides by well-defined changes in the rate of loss of sulphur. The exceptional stability of the disulphide is here confirmed by the very low gradient.

*Experimental*. The apparatus (Fig. 4) consisted of an outer vessel, A, 28 cm. long and 32 mm. wide, fitted with a lining B provided with a gutter at the bottom which served for condensing and collecting the sulphur liberated. The annular space between the tubes was closed at the top by rubber through which the tube C delivered nitrogen in order to prevent sulphur vapour passing between the tubes. A little sulphur condensed on the thin glass stirrer (which could not be removed during the runs), but this was inappreciable compared with that deposited on B.

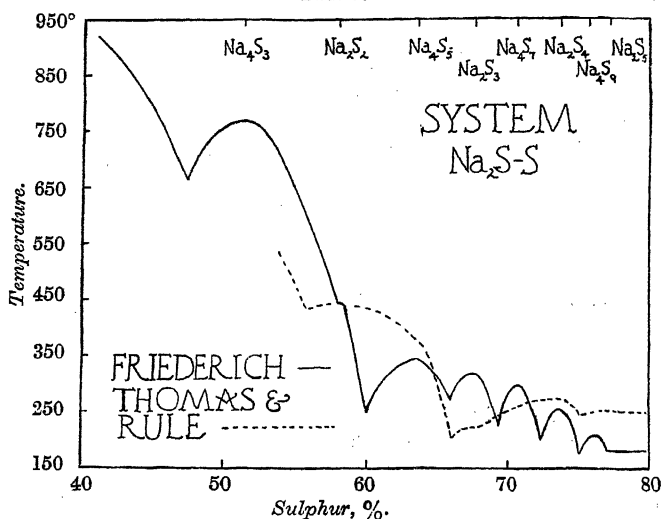
10 G. of the polysulphide were weighed into the tube and melted by heating the latter to a depth of 14 cm. in a suitable electric furnace, the temperature of which could be maintained to within  $10^\circ$  of a desired temperature. A weighed condensation tube was then pushed into position, and its upper portion cooled by a blast of

FIG. 4.



air. After 15 minutes, it was quickly removed, and replaced by a similar weighed tube. The process of weighing and replacing the tubes gave the information required. To observe the changes in rate of sulphur evolution, however, it was essential for the heating to be carefully adjusted. If the temperature was too high, the rapid decomposition prevented observation of the change in rate in materials of higher sulphur content, and if too low, the rate of evolution was impracticably slow. The results, being entirely

FIG. 5.



dependent upon the size and form of the apparatus, are only relative, but a few are given below as specimens (see Fig. 3).

At 640°.

Rate of loss of S (mg. per 15 mins.)...	3	7	10	17	22	25	28	52	60	60	60
S, %, in material ...	61.0	64.4	67.0	70.0	71.0	72.0	72.6	73.6	74.2	75.0	76.0

At 440°.

Rate of loss of S (mg. per 15 mins.) .....	15	15	15	19	58	65	98	100	100	99
S, %, in material ...	76.0	76.5	76.9	77.2	77.6	77.8	78.0	78.4	79.0	80.0

### III. The System Sodium Monosulphide-Sulphur.

This system has been studied by Friederich (*loc. cit.*) and by Rule and Thomas (J., 1917, 111, 1063). Their results, shown graphically in Fig. 5, are obviously discordant: the former obtained indications of seven compounds from well-defined maxima on the

temperature-composition curve, together with an eighth,  $\text{Na}_2\text{S}_5$ , from a hidden maximum, whilst the latter workers had evidence of di-, tri-, tetra-, and penta-sulphides, but not of compounds of the type  $\text{Na}_4\text{S}_x$ .

Both these researches are open to criticism. Friederich prepared the higher polysulphides by heating sodium carbonate and sulphur in carbon dioxide, but the material so obtained is invariably contaminated with both sulphite and sulphate, even to the extent of 20% (see p. 1484). Furthermore, his lower polysulphides, produced by dehydrating hydrated monosulphide, must also have contained salts of the sulphur oxy-acids. Neither he nor Rule and Thomas brought forward any other evidence in support of their deductions from arrest temperatures. The extreme depression of some of the eutectic points of the latter authors suggests, in the absence of any statement as to cooling rates, that these were far too rapid in view of the type of material involved.

We have obtained definite indication of di-, tetra-, and penta-sulphides and, apart from its trisulphide region, are in general agreement with the diagram of Rule and Thomas; our melting points, however, are higher in every case but one, and by as much as  $30^\circ$ .

Certain difficulties encountered in our reinvestigation call for comment. (1) There was a pronounced tendency to supercooling, particularly at certain compositions; *e.g.*, with pure sodium tetra-sulphide, this sometimes reached  $87^\circ$ , even with vigorous stirring. Traces of moisture aggravated this difficulty, and the intensely hygroscopic nature of the material rendered seeding impracticable. The only way to overcome it was to take a cooling curve with the stirrer constantly scraping the bottom of the containing vessel, remelt the contents, allow the temperature to fall slightly below the maximum temperature reached in the previous solidification, and stir and scrape vigorously. By this means results might be repeated to within  $5^\circ$ . At the solidus, supercooling was somewhat reduced by causing the stirrer to vibrate rapidly, and when this failed, recourse was had to heating curves, since Tammann's more exact method (*Z. anorg. Chem.*, 1905, 45, 24) was inadmissible.

(2) Molten polysulphides are also characterised by very slow rates of crystallisation: a melt of sodium trisulphide composition required 7 days to reach even approximate equilibrium at  $50^\circ$  below the liquidus temperature. The rates of cooling had, therefore, to be kept as low as practicable.

(3) Again, rapid change in melting points with composition between mono- and di-sulphide and above the eutectic  $\text{Na}_2\text{S}_2$ - $\text{Na}_2\text{S}_4$  renders it imperative to have precisely known compositions and

accurately determined temperatures. The runs were therefore repeated several times on each melt, and the mean temperatures of commencement and completion of solidification taken as the correct ones.

*Experimental.* The materials used for these measurements were prepared under hot toluene (see p. 1485); for those of higher sulphur content than the trisulphide, this element was added to the compound, and for those below this composition sodium was added, the mixtures being carefully melted with thorough mixing. Although this method was useful down to disulphide composition, material with less sulphur than this was difficult to melt in the quantities required, owing to the violence of the combination of such quantities of free metal with the polysulphide when the reaction temperature was reached. In such cases, small quantities of sodium were cautiously added to molten disulphide; this procedure proved perfectly satisfactory, and it is of interest that monosulphide prepared by the method of Rule and Thomas was found to have precisely the same melting point. The total weight of material obtained from a known amount of sodium served as a useful check on the triplicate sulphur and sodium analyses made of the substances after solidification. This precaution was particularly useful in those cases where segregation occurred.

Melting, according to the temperature required, was done in test tubes of Pyrex glass (25 cm. by 28 mm., and 2 mm. thick) or of glazed porcelain (20 cm. by 26 mm., and 3 mm. thick) closed by a cork or asbestos stopper which carried a stirrer (3 mm. diameter) and a thin-walled thermocouple sheath of glass or porcelain, together with a tube for the delivery of nitrogen. The quantity of polysulphide used (50 g.) allowed the thermocouple sheath to be immersed to a depth of 5 cm.

The couple used up to 600° was the "chromel-eureka" 30 S.W.G. wire of the Foster Instrument Co., Letchworth, giving one millivolt for about 12.5°. This was frequently standardised during the course of the work, ice and the boiling points of water, naphthalene, and sulphur being the reference temperatures; it proved to be remarkably constant in use. For higher temperatures, the usual platinum-platinum-rhodium junction was used; it was calibrated as above and also at the freezing points of antimony, sodium chloride, and silver. In all experiments the cold junction was surrounded by melting ice. The potential measurements involved were made in a thermocouple potentiometer ("Laboratory Pattern," by the Cambridge Instrument Co.), reading to 1 microvolt, in conjunction with a 500-ohm A. and M. galvanometer which gave a scale deflexion of 11 mm. per 0.01 millivolt. So far as actual temperature



measurements were concerned, an accuracy of  $\pm 0.025^\circ$  and  $\pm 0.20^\circ$ , respectively, may be claimed for the base and noble-metal couples. Consideration of the concordance between successive remelts, however, indicates that the operation of other factors reduces these accuracies to  $\pm 0.5^\circ$  and  $\pm 5^\circ$  respectively. Over certain regions covering a large number of melts the actual curve certainly represents an accuracy of a much higher order than this in the arrest temperature.

To ensure suitable cooling conditions, a heavily lagged, nichrome-wound furnace was made for use over the lower temperature ranges, and for the upper ranges this was placed in a sheet-iron canister which acted as an air-jacket. The cooling rates employed were approximately as follows :

	Seconds per degree at				
	1000°.	800°.	600°.	400°.	200°.
Furnace jacketed .....	1.5	2	3	5	—
Furnace unjacketed .....	—	—	17	20	40

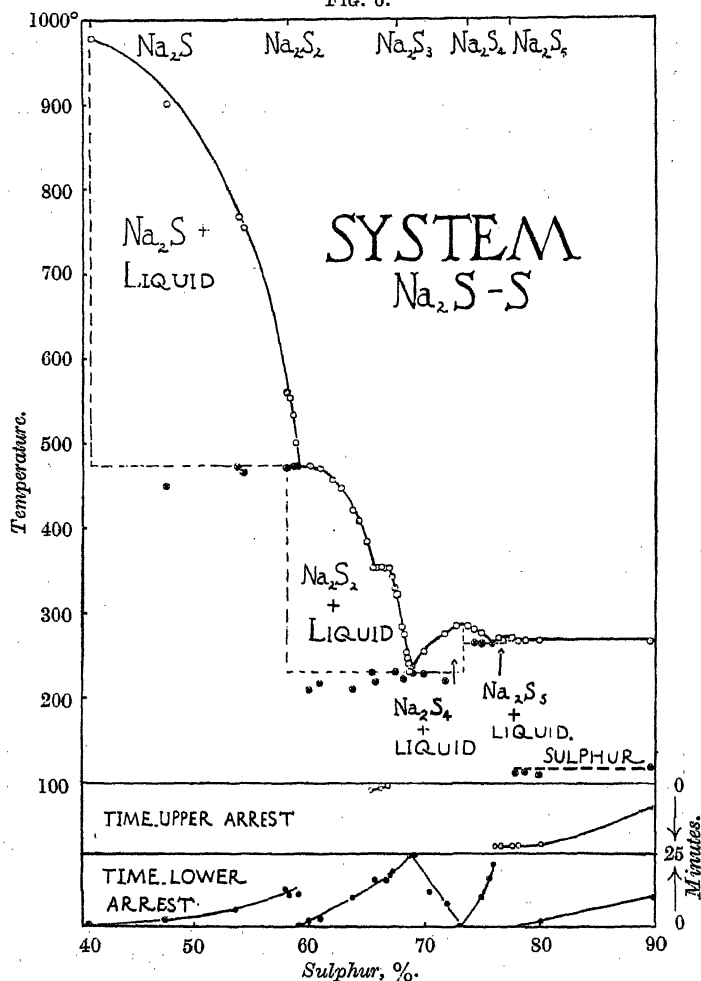
At the conclusion of each determination, the tube and its contents were allowed to reach room temperature in the furnace, the tube was broken, and a portion of the sulphide removed and immediately analysed, the remainder being stored in a sealed tube for microscopic examination.

The results are set out in Table V. The periods of arrest given in cols. 4 and 5 were obtained by plotting cooling curves in the manner described by Tammann (*Z. anorg. Chem.*, 1905, **47**, 289), but the values are only approximate since correction for supercooling cannot satisfactorily be applied. From these data, the temperature-composition diagram of the system sodium monosulphide-sulphur is plotted (Fig. 6).

The diagram begins at the melting point of sodium monosulphide ( $978^\circ$ ), which appears to be a stable compound under these conditions. From this point the curve descends steeply until disulphide proportions are reached, a break at  $473.9^\circ$  and at a composition slightly beyond that of  $\text{Na}_2\text{S}_2$  indicating that this compound is dissociated to some extent at its melting point. The almost flat portion between 58.9 and 60.2% supports this view. The break at 66.0% of sulphur, followed immediately by the flat portion to 67.0%, indicates the existence of two immiscible liquids. This is borne out by the steep descent to the eutectic which immediately follows. The liquidus curve thus gives no suggestion of sodium trisulphide. Following the  $\text{Na}_2\text{S}_2$ - $\text{Na}_2\text{S}_4$  eutectic ( $232.1^\circ$ ) at 68.77% of sulphur there is a steady rise to a maximum at tetrasulphide composition (compare Rule and Thomas), followed by the  $\text{Na}_2\text{S}_4$ - $\text{Na}_2\text{S}_5$  eutectic ( $249.2^\circ$ ) at 76.4% of sulphur, and finally

by a slight maximum at the pentasulphide composition. This is in agreement with the findings of Rule and Thomas, who suggest that the melting point of this compound is largely depressed by decomposition products. A saturated solid solution of sulphur in

FIG. 6.



pentasulphide appears at 78.5% of sulphur, as may be deduced from the constancy of the melting points ( $251.2^\circ$ ), from the gradual development of a free sulphur arrest point beyond this composition, and from the intersection of the composition-arrest period curve and the composition axis at this place. This agrees with the results

TABLE V.

S, %.	Upper arrest.	Lower arrest.	Time, upper (mins.).	Time, lower (mins.).	Solid.	Fracture.
41.00	*978°	—	—	0	Na <sub>2</sub> S	Chocolate.
47.52	900	†450.0°	—	2		
53.80	766	472.0	—	6		
54.25	755	†465.0	—	8		Light brownish-amber.
58.00	560	473.4	—	13	Na <sub>2</sub> S <sub>2</sub>	Brownish-amber.
58.25	554	475.5	—	11		
58.51	534	472.0	—	11		
58.75	501	474.8	—	11		
60.18	472.7	†210	10	2		
60.90	470.6	219	—	3		
62.04	457.6	—	5	—		
62.75	445	—	—	—		Red-brown.
63.83	420	210.6	—	10		Dark yellow, with brownish tinge.
64.35	407.5	—	—	—		
64.95	385	—	—	—		
65.51	354	*232.0	—	—		
65.71	356.4	217.2	2.5	16		
66.18	350	—	—	—		Dark yellow.
66.33	349	222	2	—		
66.55	353	—	—	—		
66.80	353	†215	1	16		
67.17	343	219.6	—	18		
67.60	330	228.8	—	19	Na <sub>2</sub> S <sub>3</sub>	
67.77	321	226.0	—	17		
68.26	285	219.0	—	—		
68.39	275	223.0	—	—		Dark yellow, with faint green tinge.
68.58	250	213	—	—		
68.59	247	223	—	—		Dark yellow, with olive-green tinge.
68.77	—	232.1	0	25		
68.99	236.1	232.1	—	25		
70.40	254.0	228.1	—	12		Deep olive-green.
71.99	275.0	217	—	8		
73.00	284.8	—	19	0		
73.96	284.8	—	21	0	Na <sub>2</sub> S <sub>4</sub>	
74.40	283.5	—	18	—		Yellowish-green.
75.10	267.0	249.0	—	10		
75.70	262.8	249.2	—	17		
76.40	—	249.2	—	22		
76.72	252.2	—	22	—		
77.77	254.0	—	22	0	Na <sub>2</sub> S <sub>5</sub>	Dark yellow.
77.92	252.2	111	22	—		
78.40	251.2	112	22	—		
80.20	251.2	†107	21	2		Light yellowish-green.
89.90	251.2	117	8	10		Grey, with yellow tinge.
94.51	250.0	119	4	20		Grey.
100.00	—	119.2	0	35		Greyish-yellow.

\* Temperature obtained from heating curve.

† Severe supercooling.

of Rule and Thomas and also with those of Küster and Heberlein (*loc. cit.*) and Jones (*loc. cit.*).

It is significant that we disagree entirely with Rule and Thomas on that portion of the curve where the upper arrest points are

particularly difficult to ascertain, *viz.*, between 64 and 69% of sulphur. The step-up in the liquidus line of their diagram between their alleged  $\text{Na}_2\text{S}_2$ - $\text{Na}_2\text{S}_3$  eutectic and trisulphide finds ready explanation in the prevalence of eutectic supercooling at these compositions. Indeed, by neglecting suitable precautions, we have been able to repeat very approximately the points recorded by these workers. Only by many repetitions, supplemented by careful heating curves, was it possible to establish the straightness of the eutectic line in this area. Nearer the disulphide it frequently failed to appear, or suffered supercooling by as much as  $45^\circ$ —an extent which makes it highly improbable that the true eutectic temperature could be reached even approximately with so little of that material present. It is noteworthy that Biltz and Wilke-Dörfurt (*Z. anorg. Chem.*, 1906, 48, 297) experienced so much difficulty in the trisulphide regions of the equilibria,  $\text{CsS-S}$  and  $\text{RbS-S}$ , that in the former case no points are given, and in the latter the curve is left discontinuous.

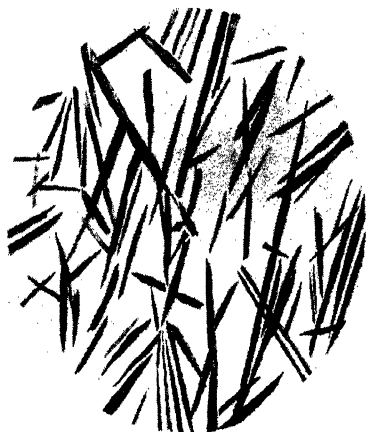
The appearance in certain melts in the region 65–69% sulphur of a small arrest at about  $190^\circ$  may have been due either to a transition or to the formation of another compound, possibly the trisulphide, only stable below about  $200^\circ$ . This phenomenon is being investigated.

*Micro-examination.* The ease with which much of the material was oxidised, and also its extremely hygroscopic nature, prevented the preparation of specimens for micro-examination by the usual means. Polishing, although difficult owing to softness and friability, was effected on various grades of emery paper under toluene or medicinal paraffin, but the polish-etch resulting was insufficient to characterise the structures present. Aqueous or ethyl-alcoholic reagents destroyed the surface, but a mixture of equal parts of amyl alcohol and carbon disulphide gave excellent results on certain specimens, notably those between disulphide and the  $\text{Na}_2\text{S}_2$ - $\text{Na}_2\text{S}_4$  eutectic and beyond pentasulphide (Plate 1, *b, d, e*). As, however, the materials were transparent, suitable sections were made by mounting them on glass slides with hot Canada balsam and rubbing them down under paraffin. Considerable patience was required, for only a very small proportion of the attempts were successful, and even these failed to realise single-crystal thicknesses or to transmit sufficient light for sharp photographic reproduction. They were, however, capable of giving a very good idea of the nature of the material, particularly if examined with the aid of oblique in addition to the normal direct illumination. The etched specimens were examined visually with oblique illumination, but here again the colour and the nature of the surfaces made successful

PLATE I.



(a)—Sodium disulphide.



(b)—64.12% Sulphur content.



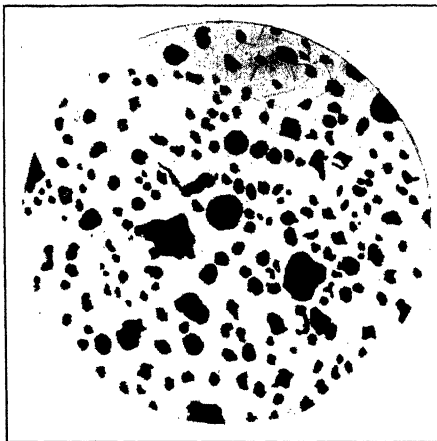
(c)—Sodium tetrathiolphide.

Magnification  $\times 80$ .

PLATE 1 (*conid.*).



(d)—78.00% Sulphur content.



(e)—89.90% Sulphur content.

Magnification  $\times 80$ .

photography particularly difficult. In both cases, permanent records were made from typical regions by a drawing and painting directly from the microscope. These faithful reproductions were photographed and appear as Plate 1 with a magnification of 80.

The monosulphide, m. p.  $978^{\circ}$  (compare m. p.  $970^{\circ}$ , Steck, Slavin, and Ralston, *J. Amer. Chem. Soc.*, 1929, 51, 3241; m. p.  $920^{\circ}$ , Friederich, *loc. cit.*), is a reddish-chocolate substance, yellowish in section, and possesses the ordinary polygonal grained structure. Melts between mono- and di-sulphide showed no evidence of any eutectic material, and thus disagree with Friederich's diagram.

The disulphide consists of characteristic transparent, light yellow, needle-like crystals frequently twinned, with straight extinction. The dark lines at the crystal boundaries in the section (Plate 1, *a*) are due to emery powder embedded in the softer eutectic material. A similar structure in yellowish-brown appeared in etching with carbon disulphide and amyl alcohol. Materials of 64.12% sulphur content etched or in section showed needle-like crystals in a ground mass (Plate 1, *b*), which could barely be resolved under high magnification on account of the thickness of the sections, but showed evidence of pearlitic intergrowths typical of eutectic material. This structure was present in proportions increasing with the diminution of the acicular constituent in specimens up to the  $\text{Na}_2\text{S}_2$ - $\text{Na}_2\text{S}_4$  eutectic. Beyond this, polygonal grains began to appear until at tetrasulphide composition the structure revealed was that associated with a metal or other homogeneous crystalline substance (Plate 1, *c*).

As the pentasulphide region was approached, the material became increasingly brittle until, at the pure pentasulphide, it was so friable that it broke down to a powder of tiny crystals on the slightest mechanical shock. This rendered polishing impossible, but a surface obtained by letting the melt slowly cool in contact with a glass slide showed homogeneous polygonal grains quartered with two dark lines across the centre. One specimen of saturated solid solution containing 78.00% of sulphur was (after thirty attempts) successfully polished and etched (Plate 1, *d*), and showed the cored structure typical of such a constituent. A section (Plate 1, *e*) from more tractable material further along the diagram shows the same solid solution in the form of spherical masses embedded in a matrix of polygonal grains of sulphur.

Without exception, these results accord well with our reinvestigation of the thermal analysis, and provide further evidence invalidating previous conclusions respecting a trisulphide and polysulphides of the tetrasodium type.

*Summary.*

A critical reinvestigation of the formation and properties of sodium polysulphides, amplified by original work, has yielded the following results.

(1) The action of sulphur on aqueous-alcoholic solutions of sodium monosulphides gives polysulphide solutions from which may be crystallised:  $\text{Na}_2\text{S}_2, 6\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_3, 8\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_4, 8\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_4, 9\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_4, 11\text{H}_2\text{O}$ ;  $\text{Na}_2\text{S}_5, 6\text{H}_2\text{O}$ ; and a tetrasulphide which may be either  $\text{Na}_2\text{S}_4, 7\text{H}_2\text{O}$  or a mixture of  $\text{Na}_2\text{S}_4, 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{S}_4, 8\text{H}_2\text{O}$ . Dehydration of the first two affords  $\text{Na}_2\text{S}_2, 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{S}_3, \text{H}_2\text{O}$  respectively.

(2) The action of sulphur on anhydrous alcoholic solutions of sodium monosulphide, although unsuited for the preparation of pure compounds, gives anhydrous di-, tri-, tetra-, and penta-sulphide.

(3) By dissolution of various proportions of sulphur in alcoholic solutions of sodium hydrosulphide, only one pure compound,  $\text{Na}_2\text{S}_4$ , is obtained:  $2\text{NaHS} + 3\text{S} \rightarrow \text{Na}_2\text{S}_4 + \text{H}_2\text{S}$ . With less sulphur the products are mixtures of tetrasulphide and unchanged hydrosulphide, with pentasulphide proportions a mixture of tetrasulphide and sulphur, and with still more sulphur possibly a higher polysulphide.

(4) The action of metallic sodium on alcoholic solutions of sodium tetrasulphide gives only the disulphide.

(5) Sulphur reacts with sodium carbonate or hydroxide at low temperatures or in solution to produce polysulphides and thio-sulphate, and at higher temperatures to give polysulphides, sulphate, and a little sulphite.

(6) Sulphur reacts with molten sodium under toluene to produce only the trisulphide.

(7) By desulphurising the polysulphides of sodium in an atmosphere of nitrogen at carefully regulated temperatures, changes in decomposition velocity indicate the existence of penta-, tetra-, and di-sulphides.

(8) A phase-rule study of the system  $\text{Na}_2\text{S}-\text{S}$  indicates that monosulphide is stable at its melting point,  $978^\circ$ ; disulphide slightly decomposes, as indicated by a hidden maximum at  $473.9^\circ$ ; tetrasulphide is stable at its melting point,  $284.8^\circ$ ; a saturated solid solution of sulphur in the pentasulphide occurs with material containing 78.5% sulphur; and finally, that tetrasodium compounds are not formed.

The peculiar stability of the tetrasulphide and the marked instability of the trisulphide have been re-affirmed.

The authors wish to acknowledge the extended loan of a potentiometer from Engineer-Commander C. J. Hawkes, R.N. (Retd.),



and a grant from the Research Committee of this College for the purchase of a similar instrument for the completion of the work. They would also warmly thank Mr. J. H. Smith, who carried out a great number of preparations and analyses, and Mr. J. Bone to whose skill the illustrations in Plate I are due.

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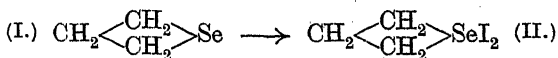
[Received, March 31st, 1930.]

### CXC.—*Heterocyclic Systems Containing Selenium.* *Part III. cycloSelenopropane.*

By GILBERT T. MORGAN and FRANCIS HEReward BURSTALL.

WHEREAS the interaction of the requisite alkylene dibromide and sodium selenide leads readily to the production in good yields of cyclic selenohydrocarbons containing five- or six-membered rings (J., 1929, 1096, 2197), yet trimethylene dibromide and sodium selenide furnish only a small proportion of *cycloSelenopropane* (I), the main product being a six-fold *polymeride* (III) resulting by aggregations of simpler four-membered unsaturated radicals,  $-\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{Se}-$ .

*cycloSelenopropane* (I), a colourless liquid with a more pungent odour than those of *cycloSelenobutane* and *cycloSelenopentane*, resembles these selenohydrocarbons in yielding a characteristic deep purple *di-iodide* (II) and a white crystalline *mercurichloride*,



but differs from the two higher cyclic homologues in its tendency to give gummy ill-defined materials.

The amorphous saponaceous *polymeride* obtained from these gummy residues decomposes on heating, but without elimination of selenium, into propylene and the more stable *cyclotrimethylene diselenide* (V). This reaction suggests that at the higher temperature the *polymeride* has undergone partial depolymerisation with the intermediate formation of *cyclohexamethylene 1:5-diselenide* (IV). Dilute nitric acid does not rupture the polymeric complex but oxidises its selenium atoms with formation of a *nitrate* (VI), a water-soluble and readily decomposable compound which by double decomposition with hydrochloric acid gives rise to the corresponding *chloride* (VII): this is reduced by sodium metabisulphite to the original *polymeride*. Hot concentrated nitric acid attacks the *polymeride*, yielding *trimethylenediselenious acid dinitrate* (VIII), and oxalic acid, the latter compound being in all probability



maintained to ensure adequate agitation and to prevent aerial oxidation. The alcoholic solution, filtered from precipitated sodium bromide and yellow gum, was distilled under diminished pressure; the distillate was rectified until a colourless alcoholic solution was obtained. This solution was then poured into a large excess of water (1000 c.c. of water for each 100 c.c. of alcoholic solution), and the aqueous-alcoholic solution repeatedly extracted with petroleum (b. p. 40–60°). The petroleum extracts were dried over calcium chloride and the solvent distilled; the residue was distilled under diminished pressure and finally rectified in a stream of carbon dioxide under ordinary pressure. A considerable quantity of the oil polymerised to a yellow gum during these distillations. *cycloSelenopropane* was thus obtained as a colourless limpid oil of exceedingly powerful and penetrating odour. The vapour has an irritant effect on the mucous membrane of the nose. It boiled at 118–119°/779 mm.;  $n_D^{15}$  1.5612;  $d_4^{20}$  1.525;  $d_4^{25}$  1.510;  $d_4^{27.5}$  1.498;  $d_4^{27}$  1.484, whence  $d_4^t = 1.554 - 0.001493t$  (Found: C, 29.2; H, 5.0; Se, 65.0.  $C_3H_6Se$  requires C, 29.7; H, 4.95; Se, 65.3%). The selenohydrocarbon was insoluble in water but was miscible in all proportions with organic media. *cycloSelenopropane* was completely volatile in the vapours of alcohol or ether and to a small extent in the vapours of other volatile solvents. It remained unchanged when kept in a cool dark place. Mineral acids caused rapid polymerisation of this cyclic selenohydrocarbon.

*cycloSelenopropane* 1:1-Di-iodide (II).—Addition of alcoholic iodine to an alcoholic solution of *cycloselenopropane* caused the separation of two products. The less soluble *material*, present in larger quantity, a polymerised condition of the di-iodide, formed an amorphous purple deposit insoluble in all organic media; it softened at 87° and then remained liquid [Found: I, 67.4.  $(C_3H_6I_2Se)_x$  requires I, 67.7%].

The more soluble monomeric *di-iodide* separated in deep purple, hair-like needles, m. p. 98°. Although soluble in acetone, benzene or chloroform, this di-iodide dissolved only sparingly in alcohol and was insoluble in cold water. It decomposed slowly on exposure to light (Found: C, 9.8; H, 1.55; Se, 20.4; I, 67.9; *M*, in acetone, 369.  $C_3H_6I_2Se$  requires C, 9.6; H, 1.6; Se, 21.1; I, 67.7%; *M*, 375).

On grinding the foregoing monomeric di-iodide with water and silver oxide a colourless neutral solution of the dihydroxide resulted, but this soon decomposed with formation of a yellow solid, m. p. 73–74°. Aqueous sodium metabisulphite reduced the di-iodide with difficulty and the presence of *cycloselenopropane* was detected by its odour. A small quantity of yellow polymeride separated slowly from solution.

*cycloSelenopropane mercurichloride*,  $C_3H_6 > Se, HgCl_2$ , separated when alcoholic solutions of mercuric chloride and *cycloselenopropane* were mixed. The white crystalline precipitate, after being washed with alcohol and dried over sulphuric acid, decomposed at  $105^\circ$  after shrinking at  $80^\circ$  (Found: Hg, 50.8; Cl, 18.4.  $C_3H_6Cl_2SeHg$  requires Hg, 51.1; Cl, 18.1%). This mercurichloride was insoluble in water and organic solvents, but aqueous caustic alkalis decomposed it, liberating *cycloselenopropane*. When heated, the mercurichloride gave mercuric selenide and trimethylene dichloride. Addition of methyl iodide to an alcoholic solution of *cycloselenopropane* and cautious evaporation of the mixture led to the production of a brown oil, from which, however, no crystalline methiodide could be isolated.

*The Polymeride (III).*—The yellow gum separating from the original alcoholic solution of *cycloselenopropane* was washed with water to remove sodium bromide and dissolved in chloroform. Evaporation of the dried solution left a deep reddish gum, which was extracted with boiling acetone until the extracts were colourless. The residual gum then solidified to a pale yellow, soap-like substance, m. p.  $38-40^\circ$  [Found: C, 29.7; H, 4.9; Se, 65.0; *M*, ebullioscopic in benzene, 738, 836.  $C_{18}H_{36}Se_6$  requires C, 29.7; H, 4.95; Se, 65.3%; *M*, 727]. This complex substance was insoluble in water or alcohol and sparingly so in acetone, but dissolved readily in warm chloroform or benzene. From its solution in the last two solvents the halogens precipitated coloured unstable additive compounds whereas methyl iodide gave a dark gum. When this *polyselenide* was gently heated, selenium was not eliminated but a considerable amount of frothing took place and the evolved gas when passed through bromine water furnished propylene dibromide, b. p.  $140-141^\circ$  (Found: Br, 78.6. Calc.: Br, 79.15%). The residue consisted of *cyclotrimethylenediselenide*, identified by comparison with an authentic specimen made by the general method of preparation for these diselenides (*v. infra*).

*The Nitrate (VI).*—Warm 2*N*-nitric acid dissolved the polymeride and deposited on cooling a white microcrystalline *nitrate*, which was washed with 2*N*-nitric acid (Found: Se, 31.8.  $C_6H_{12}O_{12}N_4Se_2$  requires Se, 32.3%). This nitrate, which dissolved readily in water to a strongly acid solution, decomposed slowly with evolution of nitrous fumes, leaving a residue of yellow gum; it decomposed rapidly at  $87^\circ$ .

The corresponding *chloride* (VII) was precipitated when concentrated hydrochloric acid was added to a solution of the foregoing nitrate (Found: C, 18.3; H, 3.3; Cl, 36.2.  $C_6H_{12}Cl_4Se_2$  requires C, 18.7; H, 3.1; Cl, 36.9%). Although moderately easily soluble

in water, this white microcrystalline chloride dissolved only sparingly in hydrochloric acid and was insoluble in alcohol or acetone. On addition of aqueous sodium metabisulphite to its aqueous solution a yellow amorphous precipitate of the polymeride was deposited.

The gummy iodide was obtained when potassium iodide solution was added to a solution of the foregoing nitrate which had been neutralised with aqueous sodium acetate. It was sparingly soluble in most common organic solvents but could not be obtained in a state of purity. It decomposed indefinitely above 100°.

Hot concentrated nitric acid reacted violently with the polymeride and the resulting clear colourless solution after evaporation and cooling deposited oxalic acid, m. p. 100° (Found: C, 18·8; H, 4·9. Calc.: C, 19·0; H, 4·8%).

*Trimethylenediselenodi-iodide* (X).—After separation of the oxalic acid the viscid residue was freed from mineral acid by sodium acetate; addition of a concentrated solution of potassium iodide then precipitated the brick-red di-iodide arising from the reducing action of hydriodic acid on trimethylenediselenious acid. *Trimethylenediselenodi-iodide*, also obtained by treating a chloroform solution of *cyclotrimethylene* diselenide with iodine, dissolved in warm chloroform or benzene but very sparingly in acetone or alcohol; it melted to a red liquid at 124° (Found: C, 8·1; H, 1·2; Se, 34·5; I, 55·7.  $C_3H_6I_2Se_2$  requires C, 7·9; H, 1·3; Se, 34·9; I, 55·9%).

*Trimethylenediselenocyanate* (IX) was readily prepared by heating trimethylene dibromide (1 mol.) and potassium selenocyanate (2 mols.) in acetone. The dark filtrate from precipitated potassium bromide was obtained as an oil which subsequently solidified and was obtained in thin colourless prisms, m. p. 53°, by crystallisation from aqueous acetone. Hagelberg (*loc. cit.*) gave m. p. 51° (Found: Se, 62·5. Calc.: Se, 62·7%). This diselenocyanate, which remained undecomposed on keeping, possessed a faint and characteristic odour.

*cyclo*Trimethylene diselenide (V), obtained as a yellow amorphous precipitate when air was aspirated through an alcoholic soda solution of the foregoing diselenocyanate, was purified by crystallisation from acetone or chloroform; m. p. 59°. Hagelberg (*loc. cit.*) gave m. p. 54·5° (Found: Se, 78·9; *M*, ebullioscopic in benzene, 225. Calc. for  $C_3H_6Se_2$ : Se, 79·1%; *M*, 200). This diselenide distilled undecomposed when heated under diminished pressure. Its chloroform solution gave with iodine a red precipitate of trimethylenediselenodi-iodide, m. p. 124° (*vide supra*).

*Trimethylenediselenious Acid Dinitrate* (VIII).—The foregoing diselenocyanate and diselenide both dissolved readily in nitric

acid and the concentrated solution deposited a mass of white needles, which were recrystallised from nitric acid (Found: Se, 40.2.  $C_3H_{10}O_{10}N_2Se_2$  requires Se, 40.4%). The dinitrate decomposed at 112°; it dissolved easily in water and this solution when treated successively with sodium acetate and potassium iodide gave a brick-red precipitate of trimethylenediselenodi-iodide, m. p. 124°.

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### CXCI.—*Pyrolysis of Diazoamino-p-toluene.*

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THE first researches on the pyrolysis of diazoamines were made by Heusler (*Annalen*, 1890, 260, 227), who heated these compounds either in sand or in liquid paraffin. Similar experiments on the heating of diazoaminobenzene in aniline were subsequently made by Hirsch (*Ber.*, 1892, 25, 1973), who recommended this process as a means of obtaining *o*- and *p*-aminodiphenyls (*o*- and *p*-xenyamines: D.R.-P. 62309; Friedländer's "Fortschritte," 3, 36; compare Aeschlimann, Lees, McClelland, and Nicklin, *J.*, 1925, 127, 66). Recent improvements in the technology of diphenyl and its derivatives have, however, afforded more direct means of preparing these two bases (Jenkins, McCullough, and Booth, *Ind. Eng. Chem.*, 1930, 22, 31; Morgan and Walls, *J. Soc. Chem. Ind.*, 1930, 49, 15r).

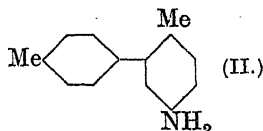
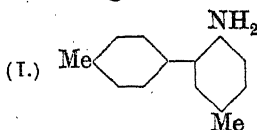
The foregoing researches showed that on pyrolysis diazoaminobenzene decomposed violently at 150°, evolving nitrogen and yielding *p*-aminoazobenzene, diphenylamine, *o*- and *p*-xenyamines, and small quantities of aniline, benzene, and diphenyl. To this list of pyrogenic products we would now add azobenzene, found in a repetition of Hirsch's experiment. In a comparative study of the pyrolysis of diazoamino-*p*-toluene and diazoamino-*p*-chlorobenzene Heusler found that both evolved nitrogen on heating, but he isolated only toluene and chlorobenzene respectively from the non-gaseous products of these decompositions, although the molecular configuration of the former diazoamine suggests that its pyrolysis should result in the production of a certain amount of *o*-aminoditolyl (I).

Pyrolysis of diazoamino-*p*-toluene in *p*-toluidine was attended by evolution of nitrogen at 150°, but in other respects the thermal changes differed considerably from those observed with diazoaminobenzene. Aminoazo-*p*-toluene and di-*p*-tolylamine were isolated only in small proportions and the total yield of aminoditolyls was

about 15% of the amount calculated. Quantitative estimations of the more volatile products of pyrolysis showed that toluene was the chief non-gaseous constituent and that nitrogen was always accompanied by ammonia.

Colouring matters such as indulines which arise in the pyrolysis of diazoaminobenzene were absent in this case. Azo-*p*-toluene was found in appreciable amount and, as this compound and toluene are both reduction products of diazoamino-*p*-toluene, the hydrogen required for their production must be sought in the resinification of a considerable proportion of the melt. The pitch left after extraction of the crystallisable products by petroleum consisted largely of acid-soluble resins similar to those obtained from low-temperature tar (*J. Soc. Chem. Ind.*, 1928, 47, 132r). The *p*-toluidine employed as solvent in the pyrolysis was recovered unchanged.

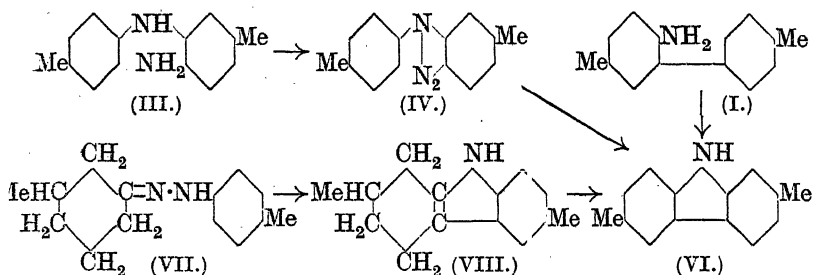
*Isomeric Aminoditolyls*.—The pyrolytic removal of nitrogen from diazoamino-*p*-toluene may be considered to yield two radicals, *p*-tolyl and *p*-iminotolyl, the union of which would result in the formation of di-*p*-tolylamine and of an aminoditolyl (I) in which the *p*-tolyl group enters the other ring in the ortho-position with respect to nitrogen.



The absence of any free para-position explains the small yield of aminoditolyl (compare Jacobsen, *Annalen*, 1922, 427, 148). The main basic product, which has been shown to have this constitution, is always accompanied by a small proportion of an isomeric amine which was first detected by its characteristic hydrochloride. Although the amount available of this by-product is too small for orientation experiments, it may be formulated provisionally as arising from the directive influence of the methyl group acting in opposition to that of the imino-residue (II). The constitution assigned to the main product, 2-amino-4' : 5-dimethyldiphenyl (4' : 5-dimethyl-2-zenylamine), was established by its pyrogenic conversion into 2 : 6-dimethylcarbazole (VI), a substance which would be a useful constitutional guide were it not for the confusion attaching to it in the literature.

2 : 6-Dimethylcarbazole.—Richter's "Lexicon" records 2 : 6-dimethylcarbazole, m. p. 208—209° (Borsche, Witte, and Bothe, *Annalen*, 1907, 359, 77), and 3 : 7-dimethylcarbazole, m. p. 224° (Ullmann, *Ber.*, 1898, 31, 1497). The alternative notation suggests

a structural identity, but as the disparity in melting points required elucidation, we have repeated the two preparations. Ullmann transformed hydrazo-*p*-toluene into the isomeric *o*-semidine (III), the triazole (IV) of which yielded 2:6-dimethylcarbazole (VI) on heating.



The *p*-tolylhydrazone (VII) of 3-methylcyclohexanone studied by Borsche, Witte, and Bothe loses ammonia to acid and becomes converted into a tetrahydrodimethylcarbazole (VIII). The constitution of this compound is not, however, defined completely by its mode of formation, since ring closure might have involved the carbon in position 2 of 3-methylcyclohexanone instead of carbon atom 6. Alternatively both condensations might have occurred concurrently with the formation of a mixture of two isomeric tetrahydrocarbazoles. However, oxidation of the product led solely to 2:6-dimethylcarbazole, m. p. 224°, identical with the two other preparations.

#### EXPERIMENTAL.

The diazoamino-*p*-toluene employed in the following experiments had been recrystallised from petroleum (b. p. 60–80°) and was in the form of yellow needles, m. p. 118°.

A preliminary heating of 10 g. of this diazoamine, which had been dried in a vacuum, with 25 g. of dry *p*-toluidine showed a slight evolution of nitrogen and ammonia at 120°, but with further rise of temperature the rate of gaseous evolution increased until at 150° the reaction became violent and exothermic, the temperature still rising without external application of heat. By operating under 5 mm. pressure, most of the *p*-toluidine present distilled away; the later fractions had a yellow tint due to azo-*p*-toluene, whereas the first runnings, when shaken with excess of 2*N*-hydrochloric acid to dissolve the base, left a light yellow, neutral oil which boiled at 110°, giving a colourless distillate identified as toluene.

**I. Quantitative Estimation of the more Volatile Products of Pyrolysis.**—(a) *Ammonia and toluene.* Quantities of diazoamino-*p*-toluene ranging from 5 to 8 g. were heated with three parts of



*p*-toluidine in a 50 c.c. distilling flask connected in series with a 10 c.c. graduated cylinder and a flask containing a measured quantity of *N*-hydrochloric acid. After the exothermic reaction had subsided, the temperature of the melt was raised until *p*-toluidine distilled. Heating was then stopped and air blown through the liquid to drive off all ammonia and toluene. The former was estimated alkalimetrically; the latter was measured directly in the graduated cylinder after the *p*-toluidine had been dissolved in 2*N*-hydrochloric acid. Calculated on a g.-mol. weight of diazoamino-*p*-toluene, the proportion of ammonia ranged from 0.31 to 0.35 g., whereas the amount of toluene varied from 40.2 to 44.1 g.

(b) *Nitrogen, ammonia and toluene.* The foregoing experimental details were modified so that the side tube of the graduated cylinder was connected with a Schiff nitrometer. One g. of the diazoamine in 4 g. of *p*-toluidine was pyrolysed in a stream of carbon dioxide and the evolved permanent gas, collected over aqueous caustic potash, was analysed and found to consist solely of nitrogen. Hydrogen either free or combined could not be detected. The weight of nitrogen from one molecular proportion of diazoamino-*p*-toluene (225 g.) was 25.8 g.

This experiment was repeated, a much larger amount (4.4 g.) of diazoamine being used. A 500 c.c. gas-holder was converted into a nitrometer, and a guard-tube, packed with dry paraffin wax to remove traces of *p*-toluidine, was inserted between the graduated receiver and the acid flask in which the ammonia was fixed as chloride. The toluene and nitrogen were measured directly, the ammonia was estimated as chloroplatinate: 225 g. of diazoamine furnished 46.5 g. of toluene, 0.31 g. of ammonia, and 26.6 g. of nitrogen, these numbers corresponding approximately with the molecular ratios of 0.5 C<sub>7</sub>H<sub>8</sub>, 0.02 NH<sub>3</sub> and 0.94 N<sub>2</sub>.

II. *Less Volatile Products of Pyrolysis.*—In earlier experiments the whole melt was distilled under reduced pressure, but experience showed that a preliminary extraction with petroleum was preferable. From two melts made by pyrolysis of 200 g. of diazoamine and 500 g. of *p*-toluidine, 482 g. of the base were recovered by distillation under reduced pressure, and when the black residue (142 g.) was extracted with excess of petroleum (b. p. 60–80°) approximately 30 g. of tarry matter remained undissolved. From this pitch a considerable amount of acid-soluble resinamine was obtained which when applied to wood surfaces from alcoholic solution gave a reddish-brown stain similar in appearance to that from the resinamines of low-temperature tar. After removal of the solvent a dark red residue (110 g.) was distilled under reduced pressure. A fraction, b. p. 74°/4 mm., consisted mainly of *p*-toluidine (22 g.), so the

whole of this base originally employed was accounted for in the distillates. The less volatile products were now distilled over a range 155—170°/4 mm., a bright red semi-solid product (57 g.) being obtained, mainly between 162° and 167°. This fraction was extracted with excess of warm 0.5*N*-hydrochloric acid; when the brownish-red residue (16 g.) was stirred with 50 c.c. of ether, 9 g. of red crystalline azo-*p*-toluene, m. p. 144° after one crystallisation from ligroin, remained undissolved. Removal of solvent from the ethereal extract yielded a semi-solid mass which gave from alcohol small characteristic red crystals of azo-*p*-toluene (1 g.) mixed with long silky needles. The less soluble azo-*p*-toluene was removed by warming the solution to 40° and filtering it rapidly; on cooling, silky yellowish-white needles (3 g.), m. p. 79°, separated from the filtrate. This product was identified as di-*p*-tolylamine and yielded a nitrosoamine crystallising from dilute alcohol in yellow needles, m. p. 101°.

6-*Amino*-3 : 4'-*dimethylazobenzene*. This substance, the chief product in the transformation of diazoamino-*p*-toluene by concentrated acid, is formed only in small quantity in the pyrolysis. Its presence could be detected in the alcoholic di-*p*-tolylamine-azo-*p*-toluene mother-liquor by a characteristic green coloration with concentrated hydrochloric acid.

In one experiment, however, a larger yield was obtained: the distillate from a melt made by pyrolysis of 267 g. of diazoamine in *p*-toluidine left after extraction with hydrochloric acid a dark brown residue (27 g.). When dry, this material was lixiviated with petroleum (b. p. 80—100°) to yield a red solution which on concentration furnished 6 g. of azo-*p*-toluene. The portion insoluble in petroleum dissolved in alcohol containing hydrochloric acid to a dark green solution, which deposited matted yellow needles (9 g.), darkening at 160° and melting at 174° (Found: Cl, 13.2, 13.5.  $C_{14}H_{15}N_3 \cdot HCl$  requires Cl, 13.5%). From this *hydrochloride*, which was hydrolysed even by water, *aminoazotoluene* was liberated by warm aqueous alkali; it crystallised from petroleum (b. p. 60—80°) in lustrous red needles, m. p. 118° (Found: N, 19.3.  $C_{14}H_{15}N_3$  requires N, 18.8%).

*Isomeric Aminoditolyls*.—The aqueous hydrochloric acid solution of primary bases (from 200 g. of diazoamino-*p*-toluene) deposited on cooling 10 g. of a hydrochloride (A) in small, thick, slightly yellow-tinted needles. Evaporation of the solution yielded a further 20 g. of these crystals. The filtrate on vigorous stirring gave a small precipitate of a hydrochloride (B) crystallising in characteristic silky needles, darkening on exposure, m. p. 175—177°, and the mother-liquor slowly furnished pale yellow, elongated plates (C), m. p. 172°.

The products B and C, which were only obtained in small amounts, yielded the same acetyl and azo- $\beta$ -naphthol derivatives. They were respectively the anhydrous and the hydrated form of the same hydrochloride (Found for B: C, 70.6; H, 7.2; N, 6.0; Cl, 14.7.  $C_{14}H_{15}N.HCl$  requires C, 71.9; H, 6.9; N, 6.0; Cl, 15.2. Found for C: C, 66.2; H, 7.6; N, 6.0; Cl, 13.9.  $C_{14}H_{15}N.HCl.H_2O$  requires C, 66.8; H, 7.2; N, 5.6; Cl, 14.1%).

The *acetyl* compound crystallised from petroleum (b. p. 80–100°) or alcohol in colourless lustrous needles, m. p. 169.5–170.5° (Found: C, 80.0; H, 7.3; N, 6.1.  $C_{16}H_{17}ON$  requires C, 80.3; H, 7.1; N, 5.9%).

The *azo- $\beta$ -naphthol* derivative crystallised from benzene, containing a little alcohol, in scarlet needles, m. p. 188–189.5° (Found: C, 81.25; H, 5.9; N, 8.2.  $C_{24}H_{20}ON_2$  requires C, 81.8; H, 5.7; N, 8.0%).

The small proportion of this aminoditolyl isolated did not permit of orientation experiments, but the more plentiful hydrochloride (A) yielded an isomeric base which was identified as follows:—

*2-Amino-4':5-dimethyldiphenyl (4':5-dimethyl-2-xenylamine)*. The hydrochloride (A), recrystallised from alcohol containing hydrochloric acid, separated in colourless needles, decomp. 216–226° (Found: N, 6.1; Cl, 15.0.  $C_{14}H_{15}N.HCl$  requires N, 6.0; Cl, 15.2%). This salt was readily diazotisable and treatment of the diazo-solution with sodium azide furnished an oily triazo-compound. The free base boiled at 165–167°/4 mm.

*2-Acetamido-4':5-dimethyldiphenyl (acetyl-4':5-dimethyl-2-xenylamine)*, prepared by the action of acetic anhydride and anhydrous sodium acetate on the foregoing hydrochloride, was only very sparingly soluble in water and crystallised from petroleum (b. p. 80–100°) in rosettes of brittle colourless needles, melting at 104° and dissolving readily in alcohol, benzene or chloroform (Found: N, 6.0.  $C_{16}H_{17}ON$  requires N, 5.9%).

*4':5-Dimethyldiphenyl-2-azo- $\beta$ -naphthol (4':5-dimethylxenyl-2-azo- $\beta$ -naphthol)* crystallised from benzene, containing a little alcohol, in lustrous red needles, m. p. 179.5° (Found: N, 7.95.  $C_{24}H_{20}ON_2$  requires N, 8.0%). This substance was almost insoluble in the alcohols, petroleum, chloroform or acetone, but dissolved readily in glacial acetic or concentrated sulphuric acid, developing with the latter a violet-red coloration.

III. *2:6-Dimethylcarbazole*.—(1) *From 4':5-dimethyl-2-xenylamine*. This oily base was heated in a hard glass tube in a current of air so that the gases passed over glowing quicklime (compare Blank, *Ber.*, 1891, 24, 306). An oily distillate (about 60%) was collected which rapidly solidified and was freed from a small amount of

unchanged primary base by crystallisation from benzene; 2 : 6-dimethylcarbazole then separated as a colourless solid, m. p. 224° (Found : C, 85.9; H, 6.55; N, 7.5.  $C_{14}H_{13}N$  requires C, 86.1; H, 6.65; N, 7.2%).

(2) *From azo-p-toluene.* This azo-compound was reduced with zinc and glacial acetic acid to hydrazo-*p*-toluene, which was transformed in alcoholic solution with stannous chloride and hydrochloric acid into the stannichloride of the *o*-semidine, 2-amino-4' : 5-dimethyldiphenylamine (Täuber, *Ber.*, 1892, 25, 1023). This readily oxidisable base was set free from the tin salt by alkali and extracted with ether, and the extract dried over anhydrous sodium sulphate. The base obtained after removal of ether crystallised from petroleum (b. p. 60—80°) in shining leaflets, m. p. 107°. Conversion into triazole was best effected by ethyl nitrite in alcoholic sulphuric acid; the product precipitated by dilution with water crystallised from petroleum in brownish-white plates, m. p. 93°. When maintained for some time at 360°, this triazole yielded 2 : 6-dimethylcarbazole (Ullmann, *loc. cit.*), which was purified by crystallisation from alcohol (with charcoal) and through its picrate (m. p. 162°).

(3) *From 3-methylcyclohexanone and p-tolylhydrazine.* In this synthesis both the racemoid 3-methylcyclohexanone and its dextrorotatory component were employed, the latter being obtained by hydrolysis of pulegone with sulphuric acid.

With *p*-tolylhydrazine the racemoid ketone gave a hydrazone liquid at the ordinary temperature, whereas the *d*-ketone gave a solid hydrazone (m. p. about 90°). On ring closure, both hydrazones gave a crystalline dimethyltetrahydrocarbazole of m. p. 147° (sintering at 135°), although this compound still retains the asymmetric carbon atom. In either case Perkin and Plant's method for tetrahydrocarbazole was employed (J., 1921, 119, 1831) in which the hydrazone was warmed with five parts of glacial acetic acid. A vigorous reaction ensued and the tetrahydro-compound separated; after recrystallisation from alcohol it was dehydrogenated by boiling with sulphur in quinoline (Perkin and Plant, J., 1923, 123, 694). The product was poured into hydrochloric acid, and the crude 2 : 6-dimethylcarbazole purified by sublimation with powdered iron at 225—240° under 15—20 mm. pressure and by crystallisation from benzene. The blue fluorescence in alcohol described by Borsche (*loc. cit.*) is not shown by solutions of the purified carbazole.

The three preparations of 2 : 6-dimethylcarbazole were shown to be identical by their consistent mixed melting points of 224°.

9-Nitroso-2 : 6-dimethylcarbazole was prepared by treating a solution of 0.8 g. of 2 : 6-dimethylcarbazole in 15 c.c. of glacial

acetic acid with a slight excess of sodium nitrite (0.6 g.) in water. The solution filled with yellow felted needles, m. p. 113° after recrystallisation from spirit.

The following table gives a comparison of the properties of carbazole (m. p. 238°), 2 : 6-dimethylcarbazole (m. p. 224°), and its 3 : 6-isomeride (m. p. 219°) (Täuber and Loewenherz, *Ber.*, 1891, 24, 1035, 2598).

Reaction.	Carbazole.	2 : 6-Dimethyl-carbazole.	3 : 6-Dimethyl-carbazole.
Picrate	M. p. 187°	M. p. 162°	M. p. 192°
Sulphuric acid with one drop of nitric acid	Blue	Yellowish-brown	Yellowish-brown
Benzoquinone in acetic acid on successive treatment with concentrated sulphuric acid, water and ether	Magenta, pale red extract	Magenta, pale red extract	Indigo-blue, blue flakes
Isatin in concentrated sulphuric acid	Indigo-blue	Indigo-blue	Indigo-blue
Chromium trioxide in sulphuric acid	Deep blue	Deep blue	No coloration
p-Nitrosophenol in concentrated sulphuric acid	Blue	Blue	—
9-Nitroso-compounds	M. p. 82°	M. p. 113°	M. p. 106°
Sulphuric acid with one drop of nitric acid.	Deep green, changed to blue.	Brown-red, deepened.	—
Hydrochloric acid to alcoholic solution (a); on warming (b)	(a) Red coloration (b) Blue flocks	(a) Indistinct coloration (b) Blue flocks	— —

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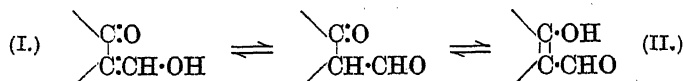
## NOTES.

*The Mechanism of Cyanoacetamide and Cyanoacetic Ester Condensations. A Reply.* By JOGENDRA CHANDRA BARDHAN.

A SHORT time ago (J., 1929, 2225) the author discussed Ingold's view (J., 1921, 119, 330) that monoketonic compounds react with ethyl cyanoacetate in the enolic form, in the light of the contrary observations of Kohler and Corson (*J. Amer. Chem. Soc.*, 1923, 45, 1975) and of Lapworth and McRae (J., 1922, 121, 2741). In a recent communication (this vol., p. 184) Ingold states that the author's account of his work on the subject is misleading inasmuch as his subsequent modified views (J., 1926, 1868) have not been taken into consideration. In this later paper Ingold's references to aldol condensation are very brief. Indeed, no mention is made of

his earlier work or of the subsequent demonstrations of Kohler, Lapworth, and others which are definitely at variance with his hypothesis. In these circumstances the omission by the author of any reference to this paper was unavoidable.

The evidence which Ingold brings forward in support of the statement that in an enolised  $\beta$ -diketone carbon coupling consistently occurs at enolic carbon is not conclusive. There can be little doubt that in ethoxymethylene-ketones and other  $\alpha\beta$ -unsaturated ketones, *e.g.*, mesityl oxide, benzylideneacetone, etc., the ethylenic double bond takes part in additive reactions; but it is not clear to the author why similar considerations would hold in the case of enolised 1:3-dicarbonyl compounds where owing to prototropic changes the enolic double bond cannot always remain in the  $\alpha\beta$ -position. Furthermore, Ingold assumes that in hydroxymethylenecyclohexanone the direction of enolisation is beyond doubt and carbon coupling takes place at the enolic carbon, leading to the formation of a quinoline derivative. So far as the author is aware, scarcely any work appears to have been done on the constitution of hydroxymethylenecyclohexanone. On general grounds it is, however, quite conceivable that equilibrium exists between the hydroxymethylene form (I) and the aldo-enolic form (II), especially as the cyclohexane ring exhibits a marked tendency to acquire a double bond (compare, for instance, Dieckmann, *Annalen*, 1901, 317, 27; Birch, Kon, and Norris, J., 1923, 123, 1368). Consequently the view that in



hydroxymethylenecyclohexanone the direction of enolisation is fixed cannot be regarded as correct. According to the author's view, the preferential formation of the quinoline derivative is explicable by the superior activity of the aldehyde group in comparison with the carbonyl. The author's observations, however, are based on only a few instances and therefore it seems desirable to postpone discussion until further experiments have been performed. —UNIVERSITY COLLEGE OF SCIENCE, CALCUTTA. [Received, May 12th, 1930.]

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*The Preparation of Anhydrous Oxalic Acid.* By ERIC IAN JOHNSON and JAMES RIDDICK PARTINGTON.

ANHYDROUS oxalic acid is readily prepared by the following method. A mixture of 5 g. of the hydrated acid with 100 c.c. of toluene, previously distilled over calcium chloride, is distilled in a wide-necked conical flask until about 15 c.c. of liquid remain. The contents of

the flask are submitted to filtration and the solid is washed with a little dry benzene. It is then kept in a vacuum desiccator over wax for 12 hours. The product is found by titration to be pure anhydrous oxalic acid. A conical flask is used since, during distillation, the anhydrous acid separates in small needles adhering to the side of the flask which are difficult to remove from an ordinary distilling flask. The method is probably capable of application, with suitable distilling liquids, in many other cases and an attempt is being made to obtain anhydrous periodic acid in this way. A similar method using carbon tetrachloride has been described (Adams, "Organic Syntheses," 1921, Vol. I, p. 67). Since toluene has a higher boiling point than carbon tetrachloride, its use will probably expedite the dehydration.—EAST LONDON COLLEGE, UNIVERSITY OF LONDON.  
[Received, May 24th, 1930.]

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**Titanium**, preparation of (VAN ARKEL and DE BOER), ii, 1193.

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*Toluene compounds Me = 1.*

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Titanic chloride, compound of acetic acid with (FICHTER and REICHART), ii, 194.

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*o*-Tolidine, preparation of solutions of (ROAKE), ii, 432.

*p*-Tolualdehyde, condensation of, with menthone (SAMDAHL), i, 414.

*o*- and *p*-Tolualdehydes *p*-nitrophenylhydrazines (STEPHEN), i, 1131.

**Toluamides**, hydroxy-, acetyl, and benzoyl derivatives (ANSCHÜTZ, ASCHENBERG, KUCKERTZ, KRONE, RIEPENKRÖGER, and ZERBE), i, 666.

**Toluene**, sorption of the vapour of, by sugar charcoal (BAKER and MCBAIN), ii, 193.

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**Toluene**, 3:5-diamino-2:4-dihydroxy-, and its tetra-acetyl derivate (HENRICH and GÖTZ), i, 913.

*p*-chloro-, photochemical action of iodine on (SILBERRAD), i, 16.

nitration of (HODGSON), i, 1397.

*p*-chlorothioli- (LECHER, HOLSCHNEIDER, KÖBERLE, SPEER, and STÖCKLIN), i, 390.

*p*-nitro-, melting point of (PUSHIN), ii, 277.

*trinitro*-, heat of fusion of (RINKENBACH and HALL), ii, 207.

2:4:6-*trinitro*-, decomposition of, by sunlight (KRAUZ and TUREK), i, 646; (WICHERT and DONAT), i, 803.

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**Toluenes**, iodo-, isomeric, polarity effects in (SHOESMITH and SLATER), i, 16.

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*o*- and *p*-nitro-, separation of (MOLINARI), i, 380.

*Toluene compounds, Me = 1.*

- Toluenes, *as-trinitro*-, reactions of (BRADY, HEWETSON, and KLEIN), i, 16.
- o*-Toluenesulphonic acid, and its derivatives, and 3-nitro- (BÜLOW and SPENGLER), i, 1102.
- p*-Toluenesulphonylformaldoxime (WALKER), i, 1193.
- p*-Toluenesulphonylformaldoxime, and its phenylcarbamate (WALKER), i, 1193.
- 4-*p*-Toluenesulphonyl-3:5-dimethylisoxazole, and 4-*m*-nitro- (BÜLOW and SPENGLER), i, 1102.
- 4-*p*-Toluenesulphonyl-3:5-dimethylpyrazole, and its salts, and 4-*m*-nitro- (BÜLOW and SPENGLER), i, 1102.
- Toluene-3-azo-oximinacetotoluidides (KARRER, DIEHMANN, and HAEBLER), i, 243.
- 4-*p*-Toluenesulphonyl-1-phenyl-3:5-dimethylpyrazole, and 4-*m*-nitro- (BÜLOW and SPENGLER), i, 1102.
- 1-*p*-Toluenesulphonyl-2-aminonaphthalene (CHARRIER, CRIPPA, TOIA, and BIANCHETTI), i, 591.
- p*-Toluenesulphenanilide (LECHER, HOLSCHNEIDER, KÖBERLE, SPEER, and STÖCKLIN), i, 390.
- p*-Toluenesulphonylbenzylamide (HOLMES and INGOLD), i, 1143.
- p*-Toluenesulphonylbenzylmethanamide, and its hydrochloride (HOLMES and INGOLD), i, 1143.
- o*-Toluenesulphonylbenzylaldehyde, and the corresponding acetates (V. AUWERS), i, 1461.
- o*-2-Toluenesulphonylbenzylmalonitrile (V. AUWERS), i, 1460.
- 1-*p*-Toluenesulphonylbenzylmalonitrile-8-sulphonic acid, and its sodium salt (FINZI), i, 654.
- Toluene-*o*-sulphonic acid, electrochemical oxidation of (FICHTER and STOCKER), i, 239.
- indazole ester (V. AUWERS), i, 1461.
- Toluene-*p*-sulphonic acid, esters, alkylation by (FINZI), i, 648.
- action of magnesium organic halides with (GILMAN and BEABER), i, 802.
- substituted phenyl and tolyl esters (SANÉ and JOSHI), i, 134.
- Toluenesulphonic acids, *d*-nitro-, sodium salts (BRADY, HEWETSON, and KLEIN), i, 16.
- d*-*o*-*p*-Toluenesulphonylpropionic acid, and its ethyl ester and amide (KENYON, PHILLIPS, and TURLEY), i, 507.
- p*-Toluenesulphonyl chloride, action of on nitrophenols (SANÉ and JOSHI), i, 134.

*Toluene compounds, Me = 1.*

- p*-Toluenesulphonylhydrazine, and its derivatives (FREUDENBERG and BLUMMEL), i, 52.
- o*-Toluenesulphonylindazoles (V. AUWERS), i, 1461.
- Toluene-*p*'-sulpho-*p*-phenetide, nitroderivatives, and their derivatives (REVERDIN), i, 1409.
- p*-Toluenethiolsulphonic acid, *o*-nitrophenyl ester (MILLER and SMILES), i, 392.
- m*-Toluic acid, 6-thiol- (KROLLFEIFFER, SCHULTZE, SCHLUMBOHM, and SOMMERMEYER), i, 1306; (ARNDT), i, 1311.
- p*-Toluic acid, 2-amino- and 2-nitro-, diethylaminoethyl esters, and their hydrochlorides (SODERMAN and JOHNSON), i, 814.
- o*-trichloro-, synthesis of (BÖSEKEN and GELISSEN), i, 30.
- Toluic acids, hydroxylamine salts (OESPER and BALLARD), i, 1233.
- Toluic acids, amino-, separation of (MAYER and SCHULZE), i, 1315.
- o*-Toluidine, 3:5-dibromo-, additive compounds of, with metallic salts (HANN and SPENCER), i, 653.
- 5-iodo-, preparation of, and its salts and derivatives (HANN and BERLINER), i, 908.
- m*-Toluidine, bromo-4:6-dihydroxy-, hydrobromide, and its derivatives (HENRICH and GÖTZ), i, 913.
- p*-Toluidine, surface tension of aqueous solutions of (EDWARDS), ii, 387.
- Toluidines hydroferriocyanides of (CUMMING), i, 122.
- detection of, colorimetrically (MURRAY), ii, 163.
- o*-*o*- and *p*-Toluidineacetophenones, hydrazones of (BUSCH, FRIEDENBERGER, and TRISCHBEIN), i, 41.
- p*-Toluidine-*p*-anisidine-1:4-naphthaquinone (FRIES and BILLIG), i, 940.
- β*-Toluidinebenzylmalonic acids, esters of (WAYNE and COHEN), i, 550.
- 3-Toluidine-5-ketoxoxazoles (WORRALL), i, 303.
- 3-Toluidine-5-ketopyrazoles (WORRALL), i, 303.
- 1-Toluidinomethylbenzothiazoles, and their derivatives (HUNTER), i, 1336.
- 2-*p*-Toluidine-1:4-naphthaquinone, 3-chloro-2-*N*-nitroso- (FRIES and BILLIG), i, 939.
- 1-*p*-Toluidine-3-naphthol-4-sulphonic acid (LANTZ and WAHL), i, 910.
- Toluidine-oximinopinacolins (RHEINBOLDT and SCHMITZ-DUMONT), i, 1132.

*Toluene compounds, Me = 1.*

- Toluidino-5-phenyl-1:3:4-thiodiazines, and their hydrobromides and derivatives (BOSE), i, 1465.
- m*-Toluidino-*m*-toluthiazole, and its derivatives (LEVI), i, 445.
- 5-Toluidino-4-*o*-tolyl-1:2:4-triazole, 3-thiol, derivatives of (FROMM and SZENDRŐ), i, 985.
- p*-Toluidino-3:4:5-trimethoxyphenylcarbinol, and its hydrochloride (SONN and MEYER), i, 932.
- p*-Toluiminoisothio-*p*-toluamide, and its hydrochloride (ISHIKAWA), i, 1149.
- p*-Toluoyl chloride, 2-nitro- (SODERMAN and JOHNSON), i, 814.
- Toluoylacetamides, hydroxy- (ANSCHUTZ, ASCHENBERG, KUCKERTZ, KRONE, RIEPENKRÖGER, and ZERBE), i, 667.
- o*-Toluoylbenzoic acid, methyl ester (WEISS and KOREZYN), i, 560.
- o*-Toluoylbenzoic acids (BRAND, LUDWIG, and BERLIN), i, 904.
- m*-Toluoylbenzoic acid, *o*-4-bromo- (HELLER and MÜLLER-BARDORFF), i, 546.
- m*-Toluoyl-3:4:5:6-tetrachloro-2-benzoic acid, 2'-hydroxy- (ORNDORFF and PATEL), i, 672.
- 8-Toluoyl- $\alpha$ -naphthoic acid (MASON), i, 33.
- $\beta$ -Toluoxyloxypropionic acids, and their amides (POWELL and JOHNSON), i, 278.
- $\gamma$ -*m*- and *p*-Toluoxyloxypropyl alcohols (POWELL and JOHNSON), i, 278.
- 2-*o*-Toluoylphenyldi-*o*-tolylcarbinol (WEISS and KOREZYN), i, 560.
- Tolquinone, action of azides with (CHATTAWAY and PARKES), i, 985.
- Tolyleneamidine-2-phenyl-*o*-carboxylic acid. See 4-Methylbenziminazole-2-benzoic acid.
- m*-Tolyl hydroxyethyl ether (CASSELLA & Co.), i, 897.
- p*-Tolyl *p*-acetoxymethyl ether (PUMMERER, PUTTFARCKEN, and SCHOPFLOCHER), i, 1263.
- isoamyl sulphide (GILMAN, BEABER, and MYERS), i, 1057.
- benzyl ether (v. BRAUN and REICH), i, 1405.
- $\beta$ -chloroethyl sulphide (LECHER, HOLSCHNEIDER, KÖBERLE, SPEER, and STÖCKLIN), i, 890.
- cinnamyl ether (CLAISEN, KREMERS, ROTH, and TIETZE), i, 656.
- methyl ether, 2-amino-, and 5-bromo-2-amino-, 2-acetyl derivatives (GRIFFITH and HOPE), i, 827.
- o*- and *p*-Tolyl acetates, action of sodium on (HALL), i, 23.
- p*-Tolylacetaldehyde *p*-nitrophenylhydrazone (STEPHEN), i, 1131.

*Toluene compounds, Me = 1.*

- o*-Tolylacetic acid,  $\omega$ -amino- and its derivatives (v. BRAUN and REICH), i, 1407.
- p*-Tolylisoamylsulphone (GILMAN, BEABER, and MYERS), i, 1057.
- o*-Tolyl anisyl ketone (DE DIESBACH and STREBEL), i, 1435.
- o*-Tolylarsinic acid (BURTON and GIBSON), i, 84.
- Tolyl-5-arsinic acids, diamino-, and nitroamino-, benzoyl derivatives (HAMILTON and MAJOR), i, 990.
- N*-*p*-Tolylbenzimid-*p*-tolyl ether (CHAPMAN), i, 1401.
- o*-Tolylbenzylketimine, and its hydrochloride (JASPERS), i, 936.
- p*-Tolylborneol (LEDUC), i, 821.
- p*-Tolylcamphene (LEDUC), i, 821.
- o*- and *p*-Tolylcarbamic acids, dinitro-, esters of (KNIPHORST), i, 906.
- o*-Tolylcarbamide, 5-iodo-, and its hydrochloride (HANN and BERLINER), i, 908.
- m*-Tolylcarbamide, 2:4- and 4:6-dinitro- (GIUA and PETRONIO), i, 1397.
- o*- and *p*-Tolylcarbamides, dinitro- (KNIPHORST), i, 906.
- o*-Tolylcarbylamine, 5-iodo- (HANN and BERLINER), i, 908.
- p*-Tolylcitronellylamine, and its derivatives (RUPE and RINDERKNECHT), i, 658.
- m*-Tolyleyanamide, 4:6-dinitro- (GIUA and PETRONIO), i, 1397.
- 1-Tolyl-3:5-diketopyrazolidines, tolylhydrazine derivatives of (VAN ALPHERN), i, 83.
- p*-Tolylidimethylaminomethyl-*p*-tolylmethane, and its hydrochloride (SOMMELET), i, 803.
- p*-Tolylidiphenyl- $\alpha$ -naphthylmethyl chloride and methyl ether (DILTHEY), i, 653.
- p*-Tolyl diphenyl ketone, and its oxime (DILTHEY), i, 653.
- $\beta$ -Tolylethylamines,  $\omega$ -chloro-, salts and derivatives of (v. BRAUN and REICH), i, 1406.
- $\alpha$ -*o*-Tolyl- $\beta$ -ethylcarbamide (KNIPHORST), i, 906.
- o*-Tolylethylketimine, and its hydrochloride (JASPERS), i, 936.
- $\alpha$ -Tolyl- $\beta\beta$ -ethylnitrocarbamides, dinitro- (KNIPHORST), i, 906.
- p*-Tolylidenemalononic acid, and its ethyl ester (CHRZASZCZEWSKA), i, 956.
- p*-Tolylidenementhone, and its hydrochloride (SAMDAHL), i, 415.
- 5-Tolylimino-4-acetyl-2-methylthiol-4:5-dihydrothiodiazole (GUHA and RAY), i, 703.

*Toluene compounds, Me = 1.*

- 1-Tolylimino- $\beta$ -naphthaquinone (SOCIÉTÉ ANONYME DES MATIÈRES COLORANTES), i, 418.
- 5-Tolylimino-2-thion-2:3:4:5-tetrahydro-1:3:4-thiadiazole, and its derivatives (GUHA and RAY), i, 703.
- o*-Tolylcycloiminotoluquinone (CHATTAWAY and PARKES), i, 935.
- 2-*p*-Tolylindazole, 3-cyano-, and its oxide (HELLE and SPIELMEYER), i, 838.
- 1-Tolylindazoles, 4-nitro- (V. AUWERS and FRESE), i, 1102.
- 2-*p*-Tolylindazole-3-carboxylic acid (HELLER and SPIELMEYER), i, 838.
- p*-Tolylmercuric hydrogen carbonate and mercaptan (KOTEN and ADAMS), i, 236.
- p*-Tolylmercuri-2:4:6-trinitrophenyl (KOTEN and ADAMS), i, 237.
- o*-Tolylmethylketimine, and its hydrochloride (JASPERS), i, 936.
- a-p*-Tolyl- $\beta\beta$ -methylnitrocarbamide, 2:6-dinitro- (KNIPPHORST), i, 907.
- 3-*m'*-Tolyl-5-methylpyrazole, 3:2'-hydroxy- (WITTIG), i, 279.
- 4-*p*-Tolylmorpholine (CRETCHER and PITTENGER), i, 228.
- Tolynaphthalimide, *o*-amino- (CHAKRAVARTI), i, 162.
- 2-Tolyl- $\alpha\beta$ -naphthatriazoles, and their oxides, and 4-hydroxy- (CHARRIER, CRIPPA, TOIA, and BIANCHESI), i, 591.
- 1-*p*-Tolyl-*lin*-naphthatriazole-4:9-quinone (FRIES and BILLIG), i, 940.
- m*-Tolyl- $\alpha$ - and - $\beta$ -naphthylamines, dinitro- (BRADY, HEWETSON, and KLEIN), i, 16.
- s-o*-Tolyl- $\alpha$ -naphthylcarbamide, 5-iodo- (HANN and BERLINER), i, 903.
- a-m*-Tolyl- $\beta$ -nitrocarbamide,  $\alpha$ :4:6-dinitro- (GIUA and PETRONIO), i, 1397.
- a-m*-Tolyl- $\alpha\beta$ -dibenzoylthane (CONANT and LUTZ), i, 682.
- a*-Tolyl- $\alpha\beta$ -dibenzoylthylenes (CONANT and LUTZ), i, 682.
- 2-*p*-Tolyl- $\alpha\beta$ -2:3-dihydro-*p*-benzoquinonemethane, and its derivatives (PUMMERER, PUTTFAROKEN, and SCHOFFLOCHER), i, 1262.
- p*-Tolyl- $\alpha\beta$ -*p*-oxodihydrobenzodiazphospholium (AUTENRIETH and BÖLLI), i, 1469.
- p*-Tolyl- $\alpha\beta$ -*p*-oxotetrahydrodiazphospholium (AUTENRIETH and BÖLLI), i, 1469.
- p*-Tolyl- $\alpha\beta$ -*p*-thiodihydrobenzodiazphospholium (AUTENRIETH and MEYER), i, 990.
- p*-Tolyl- $\alpha\beta$ -thiophosphoryl dichloride (AUTENRIETH and MEYER), i, 807.
- o*-Tolylmethylketimine, and its derivatives (JASPERS), i, 936.

*Toluene compounds, Me = 1.*

- $\gamma$ -*o*- and -*p*-Tolylpropinenes (BERT, DORIER, and LAMY), i, 1873.
- $\beta$ -*m*-Tolylpropionic acid,  $\alpha$ -cyano- (BAKER and LAPWORTH), i, 30.
- 1-*p*-Tolyl-2-pyrrolidone, and its picrate (LIPP and CASPER), i, 963.
- 3-Tolylrhodanylidene- $\Delta^{5:8}$ -oxindoles (HANN), i, 987.
- p*-Tolylselenoglycollic acid, and its salts (MORGAN and PORRITT), i, 1197.
- p*-Tolylselenoxyglycollic acid (MORGAN and PORRITT), i, 1197.
- 4-*p*-Tolylsemicarbazide, and its derivatives (WHEELER and BOST), i, 317.
- p*-Tolylsuccinic acid (CHRSZASZCZEWSKA), i, 956.
- p*-Tolylsulphonyl- $\beta$ -phenylpropionic acid (ARNDT), i, 1310.
- $\beta$ -*p*-Tolylsulphonylpropionic acid (ARNDT), i, 1310.
- $\beta$ -*p*-Tolylsulphoxypropionic acid (ARNDT), i, 1310.
- Tolyl-2-thio-4-ketothiazolidines, condensation of, with substituted vanillins (HANN), i, 1105.
- $\beta$ -*p*-Tolylthiol-*n*-butyric acid (KROLL-PFEIFFER, SCHULTZ, SCHLUMBOHM, and SOMMERMEYER), i, 1305.
- a-p*-Tolylthioldiphenylacetic acid (BISTRZYCKI and RISI), i, 1426.
- 2-*p*-Tolylthiophen (CHRSZASZCZEWSKA), i, 956.
- o*-Tolyl-*p*-tolyl ketone (DE DIESBACH and STREBEL), i, 1435.
- 4-*o*-Tolyl-1-*o*-tolylthiocarbamidophenylthiosemicarbazide (GUHA and RAY), i, 1462.
- Tomato plants, nutrition and growth of (KRAYBILL and SMITH), i, 1122.
- effect of sodium nitrate on growth of (WORK), i, 1366.
- Torulin (KINNERSLEY and PETERS), i, 1516.
- Tourmaline in Dartmoor granite (BRAMMALL and HARWOOD), i, 819.
- Toxicological analysis. See Analysis.
- Toxicology, chemical (KOHN-ABRIST), i, 1116.
- Toxins (KARRER, WEBER, and VAN SLOOTEN), i, 1226.
- conversion of, into anatoxins (BERTHELOT and RAMON), i, 481.
- Train oil, separation of unsaturated fatty acids in (TOYAMA and TSUCHIYA), i, 1129.
- Transfer resistance (FERGUSON and VAN ZYL), ii, 547.
- Transport numbers, apparatus for determination of (MACINNES and BRIGHTON; SMITH and MACINNES), ii, 542.

- Trees, descent of nitrogenous substances in leaves of, in autumn fading (COMBES), i, 1023.
- deciduous, constituents of leaves of (FRICKE), i, 764.
- Trehalose in yeast (E. M. and F. C. KOCH), i, 1508.
- iso*Trehalose, and its octamethyl ether (SCHLUBACH and MAURER), i, 888.
- Triacetoneamine, nitroso-, catalysis of decomposition of, by hydroxyl ions (BRONSTED and KING), ii, 1171.
- $\alpha$ -2:4-Triacetoxyacetophenone (NIERENSTEIN, WANG, and WARR), i, 34.
- 2:4:6-Triacetoxybenzaldehyde (PRATT and ROBINSON), i, 826.
- Triacetoxy $\delta$ -hydroxychlorodititanium chloride (GIUA and MONATH), i, 531.
- Triallylacetophenone (HALLER, BAUER, and RAMART), i, 261.
- Triallylsulphonium iodide, compound of iodoform with (STEINKOPF and Bessaritsch), i, 496.
- $\beta$ -Triamyllose nitrates (PRINGSHEIM, LEIBOWITZ, and SILMANN), i, 1244.
- Trianhydrostrophanthidin (JACOBS and COLLINS), i, 566.
- Trianhydrotetrakisdi-phenylgermanediol (MORGAN and DREW), i, 1197.
- 4:4':4''-Trianilinotri-*m*-tolylearbinol (GOMBERG and ANDERSON), i, 1065.
- 4:4':4''-Trianilinotri-*m*-tolylmethane (GOMBERG and ANDERSON), i, 1065.
- Triaquotriamminecobaltic triaquotrisulphatocobaltiate. See under Cobalt.
- Triarsenatomanganic acid (DREISS), ii, 893.
- Triarylearbinols, *o*-hydroxy-, tautomerism of (GOMBERG and MCGILL), i, 1269.
- Triazine derivatives, thermal properties of binary mixtures of (PASCAL), ii, 953.
- Triazines, preparation of (SOCIETY OF CHEMICAL INDUSTRY IN BASLE), i, 441.
- Triazinetricarboxylic acid, complex iron derivatives of (PASCAL), i, 984.
- 1:2:3-Triazole, 4:5-dicyano-, and its derivatives (GRISCHKEVITSCH-TROCHIMOVSKI; GRISCHKEVITSCH-TROCHIMOVSKI and KOTKO), i, 1104.
- 1:2:3-Triazolecarboxylic acid, cyano-, and its ethyl ester (GRISCHKEVITSCH-TROCHIMOVSKI; GRISCHKEVITSCH-TROCHIMOVSKI and KOTKO), i, 1104.
- Triazoledicarboxylic acid, *N*-hydroxy-, and its potassium hydrogen salt (WIELAND), i, 1050.
- 1:2:3-Triazole-4:5-dicarboxylic acid, inonamide of (GRISCHKEVITSCH-TROCHIMOVSKI), i, 1104.
- 3:4:5-Tribenzoyloxybenzaldehyde (SONN and MEYER), i, 932.
- 3:4:5-Tribenzoyloxybenzanilide (SONN and MEYER), i, 932.
- Tribenzylammonium iodide, compound of iodoform with (STEINKOPF and Bessaritsch), i, 495.
- triiodide (STEINKOPF and Bessaritsch), i, 497.
- Tribenzylmethyllammonium iodide, compound of iodine with (STEINKOPF and Bessaritsch), i, 495.
- 3:4:5-Tribenzoyloxybenzanilide (SONN and MEYER), i, 932.
- Tributylcarbinol (IVANOV), i, 503.
- Tributylmethane. See *n*-Butylmethane.
- Tricarboethoxyglycerol (ALLPRESS and MAW), i, 4.
- Tricarboethoxyglycerol (ALLPRESS and MAW), i, 4.
- Tri-*p*-carboxyphenylbismuthine di-chloride (SUPNIEWSKI), i, 1473.
- Tricyclene, nitration of (NAMETKIN and ZABRODIN), i, 416.
- dichloride*. See Camphane, *dichloro*.
- Tricyclo-(2,2,1,1,1,1,1,1)-dodecane-5:10:11:12-tetraone, and its derivatives (WEDEKIND, MILLER, and WEINAND), i, 510.
- Triethylamine, action of, on adipyl and  $\beta$ -methyladipyl chlorides (WEDEKIND, MILLER, and WEINAND), i, 510.
- compound of iodoform with (STEINKOPF and Bessaritsch), i, 496.
- Triethylcarbinyl iodide (MORGAN, CARTER, and DUOK), i, 877.
- Triethylene trisulphide, supposed (BENNETT and BERRY), i, 695.
- tetrasulphide, oxidation of, with potassium permanganate, and metallic salts derived therefrom (RAY), i, 352.
- Triethylphosphine, salts and derivatives from (COLLIE), i, 797.
- additive compound of carbon disulphide and (WIBAUT), i, 527.
- compounds of, with iodoform (STEINKOPF and Bessaritsch), i, 496.
- Triethylpropylphosphonium iodide (STEINKOPF and Bessaritsch), i, 496.
- Triethyltrimethylenetriamine, salts of (GRAYMORE), i, 76.
- Trimercuriaceto-*o*-tolnide acetate (ROSSI and BOCCI), i, 601.
- 3:4:5-Trimethoxyacetophenone, oxime of, and  $\omega$ -amino-, hydrochloride and  $\omega$ -oximo-, and its sodium salt (SONN, MÜLLER, BÜLOW, and MEYER), i, 932.
- 3:4:5-Trimethoxy-1- $\gamma$ -aminopropylbenzene (MERCK, WOLFES, and DÜTZMANN), i, 393.
- 1:2:6-Trimethoxyanthraquinone, 7-hydroxy- (JACOBSON and ADAMS), i, 1077.

- 1:2:6-Trimethoxy-9-anthrone, 7-hydroxy- (JACOBSON and ADAMS), i, 1077.
- 3:4:5-Trimethoxybenzaldehyde, formation of, from trimethylgallic acid (SONN and MEYER), i, 931.
- 3:4:5-Trimethoxybenz-*p*-anisidide, and its derivatives (SONN and MEYER), i, 932.
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# ERRATA.

## VOL. 126 (ABSTRACTS, 1924).

Page Line  
i, 273 26 for "KERNER" read "KIRNER."

## VOL. 128 (ABSTRACTS, 1925).

i, 30 9\* ,, "*a-cyano- $\beta$ -salicylpropionic acid*" read "*a-cyano- $\beta$ -salicylpropionic acid*," and for "*a-cyano- $\beta$ -m-tolylpropionic acid*" read "*a-cyano- $\beta$ -m-hydroxyphenylpropionic acid*."  
i, 298 14—15 ,, "*ethyl 3-aldehydo-5-methylindole-2-carboxylate*" read "*3-aldehydo-5-methylindole-2-carboxylic acid*."  
i, 495 26 ,, "*dipropylallylammonium iodide*" read "*dipropyldiallylammonium iodide*."  
i, 510 26\* ,, "MÜLLER" read "MILLER."  
i, 743 6\* Insert author's name, "S. THURLOW."  
i, 759 7, 9, 18 and 20 for "*Mercurialis*" read "*Mercurialis*."  
i, 830 16 and 18 for "*Columba*" read "*Calumba*."  
i, 881 23 for "*Glattfeld*" read "*Glattfeld*."  
i, 890 7\* ,, "N. ETSSLIN" read "H. ENSSLIN."  
i, 943 26 ,, "*hexahydrocadaline*" read "*hexahydrocadalene*."  
i, 954 15\* ,, "Nöhreu" read "Nöhren."  
i, 971 2\* ,, "*Ketonor-7-demethylo- $\psi$ -corydaline*" read "*Keto-7-demethylo- $\psi$ -corydaline*."  
i, 1010 33 ,, "*Biochem. J.*" read "*Biochem. Z.*"  
ii, 23 7\* ,, "JOUNEAUX" read "JOUNIAUX."  
ii, 59 3 ,, "GETMAN" read "GERMANN."  
ii, 65 18\* ,, "C. MÜLLER" read "E. MÜLLER."  
ii, 195 4 ,, "ADAMS" read "ADAM."  
ii, 257 5 ,, "SKOBELZYN" read "SKOBELTZYN."  
ii, 279 17 ,, "SOHENK" read "SOHENCK."  
ii, 382 1\* { for "*Maximum . . . 18 hours*," read "*The lowering of the*  
ii, 383 1, 2 { adsorptive power of silica by decreasing the water content,  
noted by other observers, was confirmed."  
ii, 763 10\* for "*I. MASSOW*" read "*I. MASSON*."  
ii, 888 22 ,, "*Thiosulphites*" read "*Thiosulphates*."  
ii, 936 18\* ,, "READ" read "REED."  
ii, 942 6 ,, "WEISENBERG" read "WEISSENBERG."  
ii, 1166 14 ,, "PUTTEN" read "PATTEN."

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INSTRUCTIONS TO ABSTRACTORS,  
GIVING THE  
NOMENCLATURE AND SYSTEM OF NOTATION  
ADOPTED IN THE ABSTRACTS

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# INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

## NOMENCLATURE AND SYSTEM OF NOTATION

### ADOPTED IN THE ABSTRACTS.

THE object of the British Chemical Abstracts is to furnish a concise account of the progress of chemical science and industry. It must be understood that as the abstracts are prepared for the information of chemists in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally, but unnecessary words such as "The," "Improvements in," "Process for the," etc., should be omitted. Where the original title is not sufficiently informative, an addition may be made in [     ], thus:

Electrochemical reduction [of nitro-compounds].

The names (with initials) of authors should be clearly written, followed by the abbreviated title of the Journal (see p. 14), the year, volume number, and first and last pages of paper, thus:

Dehydrogenation in presence of catalysts. M. G. STANTON and C. J. HOWE (J. Amer. Chem. Soc., 1926, 48, 1873-1882).—

2. Before beginning to write the abstract, the whole of the original paper must be read, in order to obtain a clear and connected idea of its contents and to form a judgment of its importance and of the scale on which the abstract should be made.

3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.

4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper. Authors' summaries or conclusions may be found useful as the basis of abstracts, but in nearly every case it will be found necessary to supplement these with data from the body of the paper.

5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's views and results. As the chief function of an abstract is to be informative, it should recount the achievements of the work, not merely its scope.

6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.

7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, reference to this should be made.

8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.

9. The abstracts, including those of Patents, should contain a record of all new compounds; the names of these are printed in italics and should therefore be underlined in MS. Crystal form need not be stated unless some special significance attaches to it, and it is not generally necessary to mention that a compound is colourless, or that a nitro-compound or picrate is yellow, etc. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. Merely qualitative statements as to solubility should as a rule be omitted. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, etc., must be given in every case unless recorded in earlier papers.

10. There is to be no duplication of abstracts in the A and B sections. When papers marked for abstraction for A contain matter of technical interest, or for B matter of purely scientific interest, this should be included in the abstract.

11. Abstractors should not attempt to deal with papers sent to them which they consider too far outside their scope. Further, they should notify the Editor if more papers are being sent to them than they can handle satisfactorily.

12. The Editor will be glad if abstractors will direct his attention to any papers which, in their opinion, merit notice and have not been abstracted, or to those papers which, although marked, do not appear to be worthy of an abstract.

13. Abstracts of patents should be based on the "Claims," supplemented where necessary by matter from the body of the specifications. Abstractors should notify the Editor if material sent to them for abstraction is insufficient for the production of an intelligible abstract, or if the patent appears to be devoid of scientific foundation. Illustrations should be used when required for a proper understanding of the invention.

In English and Foreign Patents the date is the date of application; when "a convention date" is given this should be added, thus: "Conv., 12. 9. 24." For U.S. Patents the date is that of the Official Gazette containing the claims; the date of filing should also be given thus: "Appl., 25. 6. 23"; serial numbers are not noted.

## 14. The following abbreviations are permitted:—

melting point .....	m. p.
freezing point .....	f. p.
boiling point at 240° under 35 mm. pressure .....	b. p. 240°/35 mm.
density 1.462 at 20° compared with water at 4°...	$d_4^{20}$ 1.462
observed rotation at 17° .....	$\alpha_D^{17}$
specific rotation at 17° .....	$[\alpha]_D^{17}$
specific refraction for D line at 10° .....	$n_D^{10}$
atomic weight .....	at. wt.
molecular weight .....	mol. wt.
molecule .....	mol.
gram-molecule.....	g.-mol.
atmospheres.....	atm.
with decomposition (in connexion with m. p.).....	decomp.
absolute (temperature) .....	Abs.
corrected (do.).....	corr.
gram-calories .....	cal.
kilogram-calories .....	Cal
British thermal units .....	B.Th.U.
grams .....	g.
kilograms .....	kg.
milligrams .....	mg.
centimetres .....	cm.
decimetres .....	dm.
cubic centimetres .....	c.c.
metres .....	m.
millimetres .....	mm.
normal (for solutions) .....	N
electromotive force.....	E.M.F.
potential difference.....	P.D.
for example.....	e.g.
that is .....	i.e.
namely .....	viz.
per cent. ....	%

## Nomenclature.

15. Employ names such as *sodium chloride*, *potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radical; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

16. Term compounds of metallic radicals with the OH group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

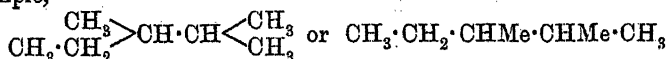
17. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen

phosphate, etc., to the acid salts. Basic salts as a rule are best designated merely by their *formulae*.

18. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO<sub>2</sub>, carbon dioxide; P<sub>4</sub>O<sub>10</sub>, phosphoric oxide; As<sub>4</sub>O<sub>6</sub>, arsenious oxide; Fe<sub>2</sub>O<sub>3</sub>, ferric oxide.

19. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter  $\alpha$  being assigned to the first carbon atom in the formula, except in the case of CN and CO<sub>2</sub>H, for example, CH<sub>3</sub>·CH<sub>2</sub>·CH<sub>2</sub>·CH<sub>2</sub>I  $\alpha$ -iodobutane, CH<sub>3</sub>·CH<sub>2</sub>·CHCl·CN,  $\alpha$ -chlorobutyronitrile.

20. Isomeric open chain compounds must be represented as substitution derivatives of the longest carbon chain in the formula; for example,



should be termed  $\beta\gamma$ -dimethylpentane, not methylethylisopropylmethane, and  $\text{CH}_3 \begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH} \end{array} \cdot \text{CH} \begin{array}{c} \diagdown \\ \text{CH}_3 \\ \text{CO}_2\text{H} \end{array}$  or CH<sub>3</sub>·CHMe·CHMe·CO<sub>2</sub>H should be termed  $\alpha\beta$ -dimethylbutyric acid, not  $\alpha\beta\beta$ -trimethylpropionic, or  $\alpha$ -methylisovaleric, or methylisopropylacetic acid.

21. Use names such as methane, ethane, etc., for the normal paraffins or hydrocarbons of the C<sub>n</sub>H<sub>2n+2</sub> series of the form CH<sub>3</sub>·[CH<sub>2</sub>]<sub>n</sub>·CH<sub>3</sub>, etc. Term the hydrocarbons C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-ine*. Adopt the name allene for the hydrocarbon CH<sub>2</sub>:C:CH<sub>2</sub>.

22. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, PhONa, etc., should be termed sodium methoxide, sodium phenoxide, etc.

23. The radicals indicated in the name of a compound are to be given in the order chloro-, bromo-, iodo-, fluoro-, nitro-, nitroso-, amino-, imino-, hydroxy-, aldehydo-, keto-, thiocyano-, acyloxy,\* alkyloxy,\* acyl,\* alkyl.\*

24. Compounds analogous to the acids of the lactic series containing the OH group should be termed *hydroxy*-derivatives, and not *oxy*-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, etc., should in like manner be termed *ethoxy*-, *phenoxy*-, *acetoxy*-derivatives. Thus  $\alpha$ -ethoxypropionic acid, OEt·CHMe·CO<sub>2</sub>H, instead of ethyl-lactic acid;

\* In these groups, closed chain radicals precede open chain radicals (e.g., benzoyl, acetyl, or phenyl, methyl); within the same section, more saturated precede less saturated (e.g., cyclohexyl, phenyl, styryl) or less complex, more complex (e.g., phenyl, naphthyl), univalent radicals precede bivalent, and so on.



3:4-diethoxybenzoic acid,  $(\text{OEt})_2\text{C}_6\text{H}_3\cdot\text{CO}_2\text{H}$ , instead of diethylprotocatechuic acid; and  $\alpha$ -acetoxypropionic acid,  $\text{OAc}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radical of protocatechuic acid by ethyl, thus,  $\text{C}_6\text{H}(\text{Et})_2(\text{OH})_2\cdot\text{CO}_2\text{H}$ , and not  $\text{C}_6\text{H}_3(\text{OEt})_2\cdot\text{CO}_2\text{H}$ , just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula  $\text{C}_6\text{HBr}_2(\text{OH})_2\cdot\text{CO}_2\text{H}$ .

25. The term *ether* should be restricted to the oxides of hydrocarbon radicals and their derivatives, and the esters should be represented by names similar to those given to metallic salts.

26. When a substituent is one of the groups  $\text{NH}_2$ ,  $\text{NHR}$ ,  $\text{NR}_2$ ,  $\text{NH}$ , or  $\text{NR}$ , its name should end in *ino*; for example,  $\beta$ -aminopropionic acid,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\beta$ -anilinoacrylic acid,  $\text{NHPh}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ ,  $\alpha$ -iminopropionic acid,  $\text{NH}:\text{CMe}\cdot\text{CO}_2\text{H}$ . When, however, the  $\text{NH}_2$  group is substituted with an acid residue such as acetyl it becomes acetamido, etc.

27. Compounds of the radical  $\text{SO}_3\text{H}$  should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

28. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteins, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide, or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

29. The Chemical Society's Collective Index (1913-1922) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

### Notation.

30. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

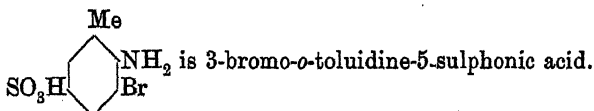
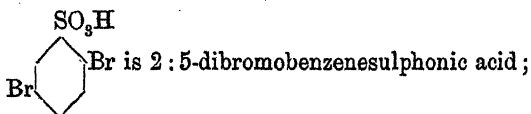
31. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

32. To economise space, it is desirable:

- (a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicals, whenever this does not interfere with the clearness of the formula.
- (b) That formulæ should be shortened by the judicious employment of the symbols Me for  $\text{CH}_3$ , Et for  $\text{C}_2\text{H}_5$ , Pr<sup>a</sup> for  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3$ , Pr<sup>s</sup> for  $\text{CH}(\text{CH}_3)_2$ , Bu for  $\text{CH}_2\cdot[\text{CH}_2]_3$ , Ph for  $\text{C}_6\text{H}_5$ , Ac for  $\text{CO}\cdot\text{CH}_3$ , and Bz for  $\text{CO}\cdot\text{C}_6\text{H}_5$ .
- (c) That formulæ should be written *in one line* whenever this can be done without obscuring their meaning.

33. In representing the constitution of benzene derivatives, the relative positions of the radicals in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

- (a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.
- (b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radical of each of these parent substances is to be regarded as in position 1 (compare Chemical Society's Collective Index).
- (c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—



34. In representing the constitution of derivatives of other cyclic hydrocarbons, graphic formulæ should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (3rd edition, 1910, pp. 14—26) should be used, pending the adoption of a scheme by the International Committee.

35. Attention is directed to the list of physico-chemical symbols on pp. 10–13, which should be used whenever possible, and also to the list of radicals which appears at the end of the Chemical Society's Collective Index.

#### Manuscript.

36. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts must be written on quarto paper (8×10 in.).

37. Each abstract, however short, should be written on a separate sheet.

38. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

39. The name of the abstractor must be written at the end of the abstract.

40. Abstracts, whether in typescript or MS., should have a wide margin at the left side and sufficient space between the lines for insertion of corrections.

**Proofs.**

41. Abstractors are expected to read and correct proofs carefully, and to check all names, formulæ, and figures against MSS.

42. All proofs, however small, must be returned to the Editor not later than 24 hours after receipt from the printers.

\* \* The Editor's decision, in all matters connected with the Abstracts, must be considered final.

*List of Physico-chemical Symbols adopted by the Chemical Society.*

[See J.C.S., 1921, 119, 502—512.]

1. *Mathematical Symbols.*

	Usual symbol.	Alternative symbol.
Base of natural (Napierian) logarithms ...	$e$	
Diameter .....	$d$	
Radius .....	$r$	
Ratio of circumference to diameter .....	$\pi$	
Summation .....	$\Sigma$	
Variation .....	$\delta$	
Total differential .....	$d$	
Partial differential .....	$\partial$	

2. *Universal Constants.*

Acceleration due to gravity .....	$g$	
Mechanical equivalent of heat .....	$J$	
Avogadro's constant [number of molecules in 1 gram-molecule (mole)] .....	$N$	
Gas constant per mole .....	$R$	
Faraday's constant (number of coulombs per gram-equivalent of an ion) .....	$F$	
Charge on an electron .....	$e$	

3. *General Physics and Chemistry.*

Length .....	$l$	
Height .....	$h$	
Mass .....	$m$	
Time .....	$t$	
Volume .....	$v, V$	
Density (mass per unit volume) .....	$d$	$D$
Pressure .....	$p, P$	
Concentration .....	$c, C$	
Mole fraction .....	$x$	
Critical constants: pressure, volume, tem- perature (centigrade), temperature (absolute), density .....	$\left\{ \begin{array}{l} p_c, v_c, \\ t_c, T_c, \\ d_c \end{array} \right.$	
Reduced quantities: pressure, volume, temperature, density .....	$\left\{ \begin{array}{l} p_r, v_r, \\ t_r, T_r, d_r \end{array} \right.$	
van der Waals's constants .....	$a, b$	
Fluidity .....	$\phi$	
Viscosity .....	$\eta$	
Surface tension .....	$\gamma$	$\sigma$
Diffusion coefficient .....	$\Delta$	
Atomic weight .....	$A$	
Molecular weight .....	$M$	
Velocity coefficient of reaction .....	$k$	
Equilibrium constant .....	$K, (K_c, K_p)$	
van't Hoff coefficient .....	$i$	
Degree of dissociation (electrolytic, thermal, etc.) .....	$\alpha$	

## 4. Heat and Thermodynamics.

	Usual symbol.	Alternative symbol.
Temperature (centigrade) .....	$t$	$\theta$
Temperature (absolute) .....	$T$	
Critical temperature .....	$t_c, T_c$	
Reduced temperature .....	$t_r, T_r$	
Critical solution temperature .....	$t_{cs}, T_{cs}$	
Quantity of heat .....	$Q$	
Entropy .....	$S$	
Specific heat .....	$c$	
Specific heat at constant pressure .....	$c_p$	
Specific heat at constant volume .....	$c_v$	
Ratio of specific heats, $c_p : c_v$ .....	$\gamma$	
Molecular heat .....	$C$	
Molecular heat at constant pressure .....	$C_p$	
Molecular heat at constant volume .....	$C_v$	
Latent heat per gram .....	$l$	
Latent heat per mole .....	$L$	
Maximum work (diminution of free energy) .....	$A$	

## 5. Optics.

Wave-length of light .....	$\lambda$	
Refractive index .....	$n$	$n_r$
Specific refractive power (Gladstone and Dale) .....	$r_G, [r_G]_\lambda$	
Specific refractive power (Lorentz and Lorenz) .....	$r_L, [r_L]_\lambda$	
Molecular refractive power .....	$\left\{ \begin{array}{l} R_G, R_L \\ [R_G]_\lambda, [R_L]_\lambda \end{array} \right.$	
Angle of optical rotation .....	$\alpha$	
Specific rotatory power .....	$[\alpha]$	
Molecular rotatory power .....	$M[\alpha]$	
Specific magnetic rotation .....	$[\omega]$	
Molecular magnetic rotation .....	$M[\omega]$	

## 6. Electricity and Magnetism.

Quantity of electricity .....	$Q$	
Current intensity .....	$I$	
Resistance .....	$R$	$W$
Electromotive force .....	$E$	
Electrode potential, or discharge potential of an ion .....	$E$	$e$
Electrode potential referred to the normal hydrogen or normal calomel electrode respectively, the potential of which is taken as zero .....	$E_h, E_c$	$e_h, e_c$
Normal potential, i.e., the electrode potential referred to the normal hydrogen or normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration .....	${}_0E_h, {}_0E_c$	${}_0e_h, {}_0e_c$
Dielectric constant .....	$\epsilon$	
Conductivity (specific conductance) .....	$\kappa$	
Equivalent conductivity .....	$\Lambda$	
Equivalent conductivity at different dilutions—volumes in litres containing 1 gram-equivalent .....	$\Lambda_{100}, \Lambda_v, \Delta_{\infty}$	

6. *Electricity and Magnetism*—(continued).

	Usual symbol.	Alternative symbol.
Equivalent conductivity of kation and of anion .....	$\Lambda_k, \Lambda_a$	
Equivalent conductivity of specified ions...	$\Lambda_K, \Lambda_{Cl}$	
Molecular conductivity .....	$\mu$	
Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm. ....	$U_k, U_a$	
Transport number of kation and of anion ...	$n_k, n_a$	
Magnetic permeability .....	$\mu$	
Magnetic susceptibility .....	$\kappa$	

*List of Symbols, Arranged Alphabetically.*

Symbol.	Name of quantity.
$A$	Atomic weight; maximum work.
$a$	Van der Waals's constant.
$b$	Van der Waals's constant.
$C$	Concentration; molecular heat.
$c$	Concentration; specific heat.
$C_p, C_v$	Molecular heat at constant pressure, and at constant volume.
$c_p, c_v$	Specific heat at constant pressure, and at constant volume.
$D$	Alternative symbol for density.
$d$	Diameter; total differential; density.
$d_c$	Critical density.
$d$	Reduced density.
$E$	Electromotive force; electrode potential.
$e$	Base of Napierian logarithms; charge on an electron.
$E_h, E_c$	Electrode potential referred to the normal hydrogen or the normal calomel electrode, respectively, the potential of which is taken as zero.
${}_0E_h, {}_0E_c$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration.
$F$	Faraday's constant (number of coulombs per gram-equivalent of an ion).
$g$	Acceleration due to gravity.
$h$	Height.
$I$	Current.
$i$	Van't Hoff's coefficient.
$J$	Mechanical equivalent of heat.
$K$	Equilibrium constant.
$K_c, K_p$	Equilibrium constant, when molar concentrations and partial pressures respectively are employed.
$k$	Velocity coefficient of reaction.
$L$	Latent heat per mole.
$l$	Length; latent heat per gram.
$M$	Molecular weight.
$M[\alpha]$	Molecular rotatory power.
$M[\omega]$	Molecular magnetic rotatory power.
$m$	Mass.
$N$	Avogadro's constant (Loschmidt's number) or number of molecules in 1 gram-molecule.
$n$	Refractive index.

*List of Symbols, Arranged Alphabetically—(continued).*

Symbol.	Name of quantity.
$n_k, n_a$	Transport number of kation and of anion.
$n_r$	Refractive index (alternative symbol).
$P$	Pressure.
$p$	Pressure.
$p_c, p_r$	Critical pressure : reduced pressure.
$Q$	Quantity of heat; quantity of electricity.
$R$	Gas constant per mole; electrical resistance.
$R_G, R_L$	Molecular refractive power, according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
$r$	Radius.
$r_G, r_L$	Specific refractive power according to Gladstone and Dale, and to Lorentz and Lorenz respectively.
$S$	Entropy.
$T$	Absolute temperature.
$T_c$	Critical temperature (on the absolute scale).
$T_r$	Reduced temperature (absolute).
$T_{cs}$	Critical solution temperature (absolute).
$t$	Time; temperature (centigrade).
$t_c$	Critical temperature (centigrade).
$t_{cs}$	Critical solution temperature (centigrade).
$t_r$	Reduced temperature (centigrade).
$U_k, U_a$	Velocity of kation and of anion in cm./sec. when the potential gradient is 1 volt per cm.
$V$	Volume.
$v$	Volume.
$v_c, v_r$	Critical volume : reduced volume.
$W$	Electrical resistance (alternative symbol).
$x$	Mole fraction.
$\alpha$	Degree of dissociation (electrolytic, thermal, etc.); angle of optical rotation.
$[\alpha]$	Specific rotatory power.
$\gamma$	Surface tension; ratio of specific heats.
$\Delta$	Diffusion coefficient.
$\delta$	Variation.
$\partial$	Partial differential.
$\epsilon$	Electrode potential (alternative symbol); dielectric constant.
$\epsilon_h, \epsilon$	Electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, the potential of which is taken as zero (alternative symbols).
$0\epsilon_h, 0\epsilon$	Normal potential, that is, the electrode potential referred to the normal hydrogen or the normal calomel electrode respectively, when the solution is molecular-normal in respect of all participating substances and ions of variable concentration (alternative symbols).
$\eta$	Viscosity.
$\theta$	Temperature (centigrade), (alternative symbol).
$\kappa$	Specific conductance (conductivity); magnetic susceptibility.
$\Lambda$	Equivalent conductivity.
$\Lambda_{10}, \Lambda_v, \Lambda_{\infty}$	Equivalent conductivity at different dilutions (volumes in litres containing 1 gram-equivalent).
$\Lambda_k, \Lambda_a$	Equivalent conductivity of kation and of anion.
$\lambda$	Wave-length of light.
$\mu$	Molecular conductivity; magnetic permeability.
$\pi$	Ratio of circumference to diameter.
$\Sigma$	Summation.
$\sigma$	Surface tension (alternative symbol).
$\phi$	Fluidity.
$[\omega]$	Specific magnetic rotation.

## JOURNALS FROM WHICH ABSTRACTS ARE MADE.

The following is a list of Journals from which abstracts are made (directly or indirectly) by the Bureau of Chemical Abstracts.

ABBREVIATED TITLE.	JOURNAL.
Abh. Böhm. Akad. . . . .	Abhandlungen der Böhmischen Akademie.
Abh. Deut. Naturwiss. Med. Ver. Böhmen	Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmen.
Acta Phytchim. . . . .	Acta Phytchimica.
Acta. Sci. Fennicae . . . .	Acta Societatis Scientiarum Fennicae.
Agric. Bull. F. M. S. . . .	Agricultural Bulletin of the Federated Malay States.
Agric. J. India . . . . .	Agricultural Journal of India.
Agric. Res. Inst., Pusa, Rep. (Bull.)	Agricultural Research Institute, Pusa, Report and Bulletins.
Allgem. Z. Bierbrau. . . .	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Amer. J. Bot. . . . .	American Journal of Botany.
Amer. J. Dis. Children . . .	American Journal of Diseases of Children.
Amer. J. Pharm. . . . .	American Journal of Pharmacy.
Amer. J. Physiol. . . . .	American Journal of Physiology.
Amer. J. Publ. Health . . .	American Journal of Public Health.
Amer. J. Sci. . . . .	American Journal of Science.
Amer. Min. . . . .	American Mineralogist.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Fís. Quím. . . . .	Anales de la Sociedad Española de Física y Química.
Analyst . . . . .	Analyst.
Annalen . . . . .	Justus Liebig's Annalen der Chemie.
Ann. Bot. . . . .	Annals of Botany.
Ann. di Bot. . . . .	Annali di Botanica.
Ann. Chim. . . . .	Annales de Chimie.
Ann. Chim. Analyt. . . . .	Annales de Chimie Analytique et de Chimie Appliquée.
Annali Chim. Appl. . . . .	Annali di Chimica Applicata.
Ann. Falsif. . . . .	Annales des Falsifications.
Ann. hyg. pub. méd. légale	Annales d'hygiène publique et de médecine légale.
Ann. Inst. Pasteur . . . .	Annales de l'Institut Pasteur.
Ann. Physik . . . . .	Annalen der Physik.
Ann. Physique . . . . .	Annales de Physique.
Ann. R. Staz. Chim. Agrar. Sperim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
Ann. sci. Univ. Jassy . . .	Annales scientifiques de l'Université de Jassy.
Ann. Soc. Geol. Congo . . .	Annales de la Société géologique de Belgique: Publications relatives au Congo Belge.
Apoth.-Ztg. . . . .	Apotheker-Zeitung.
Arb. Gebiet. Physik, Math., Chem.	Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.
Arch. Entw.-mech. Org. . .	Archiv für Entwicklungsmechanik der Organismen.
Arch. exp. Path. Pharm. . .	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Farm. speriment. Sci. aff.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Fisiol. . . . .	Archivio di Fisiologia.
Arch. Int. Med. . . . .	The Archives of Internal Medicine.
Arch. ital. Biol. . . . .	Archives italiennes de Biologie.



ABBREVIATED TITLE.	JOURNAL.
Arch. Med. Pharm. milit.	Archives de Médecine et de Pharmacie militaires.
Arch. Néerland.	Archives Néerlandaises de sciences exactes et naturelles.
Arch. Néerland. physiol.	Archives Néerlandaises de physiologie de l'homme et des animaux.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arch. Suikerind. Ned.-Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Arkiv Kemi, Min., Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J.	Astrophysical Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia Nazionale dei Lincei.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Ist. Veneto Sci.	Atti del Reale Istituto Veneto di Scienze, Lettere ed Arti.
Beitr. Min. Japan	Beiträge zur Mineralogie von Japan.
Berg-Hüttenm. Rundsch.	Berg- und Hüttenmannisches Rundschau.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Oberhess. Ges. Natur. Heilkunde	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Giessen.
Ber. Ohara Inst. landw. Forsch.	Berichte des Ohara Instituts für landwirtschaftliche Forschungen.
Ber. Sächs. Akad. Wiss.	Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.
Berlin. Klin. Woch.	Berliner Klinische Wochenschrift.
Bied. Zentr.	Biedermann's Zentralblatt.
Biochem. J.	Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Bol. Acad. Nac. Ciencias, Cordoba	Boletín de la Academia Nacional des Ciencias, Cordoba.
Boll. Chim. farm.	Bolletino Chimico farmaceutico.
Boll. Soc. Geol. Ital.	Bolletino della Società Geologica Italiana.
Boll. Soc. Med.-Chirurg.	Bolletino della Società Medico-Chirurgica, Pavia.
Bot. Centr.	Botanisches Centralblatt.
Bot. Gaz.	Botanical Gazette.
Brass. Malt.	Brasserie et Malterie.
Brau- u. Malzind.	Brau- u. Malzindustrie.
Braunkohle	Braunkohle.
Brennstoff-Chem.	Brennstoff-Chemie.
Brewers' J.	Brewers' Journal.
Brit. J. Phot.	British Journal of Photography.
Brit. Med. J.	British Medical Journal.
Buletinul Chim.	Buletinul Chimie.
Bul. Soc. Chim. România	Buletinul Societății de Chimie din România.
Bul. Soc. Romane Stiin.	Buletinul Societății Romane de Științe.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Bureau of Standards	Bulletin of the Bureau of Standards (U.S.A.).
Bull. Com. Géol. Finlande	Bulletin de la Commission Géologique de Finlande.
Bull. Forest Exp. Stat. Meguro	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
Bull. gén. Thérap.	Bulletin général de Thérapeutique médicale, chirurgicale, obstétricale.

ABBREVIATED TITLE.	JOURNAL.
Bull. Geol. d'Alsace . . .	Bulletin du Service de la Carte Geologique d'Alsace et de Lorraine.
Bull. Geol. Inst. Univ. Upsala	Bulletin of the Geological Institution of the University of Upsala.
Bull. Geol. Soc. Amer. . .	Bulletin of the Geological Society of America.
Bull. Geol. Survey, U.S.A.	Bulletin of the U.S. Geological Survey.
Bull. Geol. Survey, West Australia	Bulletin of the Geological Survey, West Australia.
Bull. Imp. Inst. . . .	Bulletin of the Imperial Institute.
Bull. Indian Ind. Lab. . .	Bulletin of Indian Industries and Labour.
Bull. Inst. Phys. Chem. Res., Japan.	Bulletin of the Institute of Physical and Chemical Research, Japan (Rikwagaku Kerkyujo Ihô).
Bull. Johns Hopkins Hospital	Bulletin of the Johns Hopkins Hospital.
Bull. School Mines and Met., Univ. Missouri . .	Bulletin of the School of Mines and Metallurgy, University of Missouri.
Bull. Sci. Pharmacol. . .	Bulletin des Sciences Pharmacologiques.
Bull. Soc. chim. . . .	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg. . .	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol. . .	Bulletin de la Société de Chimie biologique.
Bull. Soc. d'Encour. . . .	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
Bull. Soc. franç. Min. . .	Bulletin de la Société française de Minéralogie.
Bull. Soc. Franç. Phot. . .	Bulletin de la Société Française de Photographie.
Bull. Soc. Géol. Belg. . .	Bulletin de la Société Géologique de Belgique.
Bull. Soc. Ind. Mulhouse .	Bulletin de la Société Industrielle de Mulhouse.
Bull. Soc. Ind. Nord . . .	Bulletin de la Société Industrielle du Nord de la France.
Bull. Soc. Oural. Sci. Nat.	Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.
Bull. Soc. Pharm. Bordeaux	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull. Wellcome Trop. Res. Lab.	Bulletin of the Wellcome Tropical Research Laboratory.
Cairo Sci. J. . . . .	Cairo Scientific Journal.
Canada Dept. Mines Publ. .	Canada Department of Mines Publications.
Canadian Chem. Met. . . .	Canadian Chemistry and Metallurgy.
Canadian Med. Assoc. J. . .	Canadian Medical Association Journal.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
Casopis Math. Fysiky . . .	Časopis pro pěstování Matematiky a Fysiky.
Cellulosechem. . . . .	Cellulosechemie.
Centr. Min. . . . .	Centralblatt für Mineralogie, Geologie und Paläontologie.
Chem. App. . . . .	Chemische Apparatur.
Chem. Erde . . . . .	Chemie der Erde.
Chem. and Ind. . . . .	Chemistry and Industry.
Chem. Ind. . . . .	Chemische Industrie.
Chem. Listy . . . . .	Chemické Listy pro Vědu a Průmysl. Organ de la "Česká chemická Společnost pro Vědu a Průmysl."
Chem. and Met. Eng. . . .	Chemical and Metallurgical Engineering.
Chem. News . . . . .	Chemical News.
Chem. Trade J. . . . .	Chemical Trade Journal.
Chem. Umschau . . . . .	Chemische Umschau auf dem Gebiete der Fette, Öle, Wachse, und Harze.
Chem. Weekblad. . . . .	Chemisch Weekblad.
Chem.-Ztg. . . . .	Chemiker-Zeitung.
Chem. Zentr. . . . .	Chemisches Zentralblatt.
Chim. et Ind. . . . .	Chimie et Industrie.
Collegium . . . . .	Collegium.

ABBREVIATED TITLE.	JOURNAL.
Compt. rend. . . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol. . . . .	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Compt. rend. Trav. Lab. Carlsberg . . . . .	Comptes rendus des Travaux du Laboratoire Carlsberg.
Dept. Chem. S. Australia, Bull. . . . .	Department of Chemistry, South Australia, Bulletins.
Deut. med. Woch. . . . .	Deutsche medizinische Wochenschrift.
E.P. . . . .	English Patent.
Econ. Geol. . . . .	Economic Geology.
Econ. Proc. Roy. Dubl. Soc. . . . .	Economic Proceedings of the Royal Dublin Society.
Engineering . . . . .	Engineering.
Eng. and Min. J. . . . .	Engineering and Mining Journal.
Exper. Stat. Rec. . . . .	Experiment Station Record.
F.P. . . . .	French Patent.
Farben-Ztg. . . . .	Farben-Zeitung.
Fermentforsch. . . . .	Fermentforschung.
Feuerungstechnik . . . . .	Feuerungstechnik.
Flora . . . . .	Flora.
Földtani Közlöny . . . . .	Földtani Közlöny.
G.P. . . . .	German Patent.
Gas J. . . . .	Gas Journal.
Gas- u. Wasserfach . . . . .	Gas- und Wasserfach.
Gas World . . . . .	Gas World.
Gazzetta . . . . .	Gazzetta chimica italiana.
Geol. För. Förh. . . . .	Geologiska Föreningens i Stockholm Förhandlingar.
Geol. Mag. . . . .	Geological Magazine.
Gerber . . . . .	Gerber.
Giorn. Chim. Ind. Appl. . . . .	Giornale di Chimica Industriale ed Applicata.
Gummi-Ztg. . . . .	Gummi-Zeitung.
Handl. Vijft. Nat. . . . .	Handelingen van het Vijftende Natuur.
Hawaii Agric. Exp. Stat. Bull. . . . .	Hawaii Agricultural Experiment Station Bulletins.
Heart . . . . .	Heart.
Helv. Chim. Acta . . . . .	Helvetica Chimica Acta.
Indian J. Med. Res. . . . .	Indian Journal of Medical Research.
India-rubber J. . . . .	India-rubber Journal.
Ind. Eng. Chem. . . . .	Industrial and Engineering Chemistry.
Int. Rev. Sci. Pract. Agric. . . . .	International Review of the Science and Practice of Agriculture.
Int. Sugar J. . . . .	International Sugar Journal.
Iron Steel Inst. Carnegie Schol. Mem. . . . .	Iron and Steel Institute, Carnegie Scholarship Memoirs.
J.C.S. . . . .	Journal of the Chemical Society.
Jahrb. geol. Reichsanst. . . . .	Jahrbuch der geologischen Reichsanstalt.
Jahrb. Min. . . . .	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie.
Jahrb. Min. Beil.-Bd. . . . .	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie, Beilage-Band.
Jahrb. Radioaktiv. . . . .	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot. . . . .	Jahrbuch für wissenschaftliche Botanik.
Jahresber. Ges. vaterl. Kultur . . . . .	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.
Japan. J. Med. Sci. . . . .	Japanese Journal of Medical Sciences.
Japan. J. Phys. . . . .	Japanese Journal of Physics.
Jernk. Ann. . . . .	Jernkontorets Annaler.
J. Agric. Res. . . . .	Journal of Agricultural Research.
J. Agric. Sci. . . . .	Journal of Agricultural Science.
J. Amer. Ceram. Soc. . . . .	Journal of the American Ceramic Society.

ABBREVIATED TITLE.	JOURNAL.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Canad. Min. Inst.	Journal of the Canadian Mining Institute.
J. Chem. Ind. Tokyo	See Kōgyō-Kwagaku-Zasshi.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chem. Soc. Japan.	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi.)
J. Chim. phys.	Journal de Chimie physique.
J. Coll. Agric. Hokkaido	Journal of the College of Agriculture, Hokkaido Imperial University, Japan.
J. Coll. Agric. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo, Japan.
J. Coll. Eng. Tokyo	Journal of the College of Engineering, Imperial University of Tokyo.
J. Coll. Sci. Tokyo	Journal of the College of Science, Imperial University of Tokyo.
J. Exp. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Gen. Physiol.	Journal of General Physiology.
J. Genetics	Journal of Genetics.
J. Geol.	Journal of Geology.
J. Geol. Soc. Tokyo	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
J. Hygiene	Journal of Hygiene.
J. Indian Chem. Soc.	Quarterly Journal of the Indian Chemical Society.
J. Indian Ind. Lab.	Journal of Indian Industries and Labour.
J. Indian Inst. Sci.	Journal of the Indian Institute of Science.
J. Ind. Hygiene	Journal of Industrial Hygiene.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Inst. Metals	Journal of the Institute of Metals.
J. Inst. Petroleum Tech.	Journal of the Institution of Petroleum Technologists.
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute.
J. Jap. Ceram. Assoc.	Journal of the Japanese Ceramic Association.
J. Landw.	Journal für Landwirtschaft.
J. Marine Biol. Assoc.	Journal of the Marine Biological Association of the United Kingdom.
J. Med. Res.	Journal of Medical Research.
J. Min. Agric.	Journal of the Ministry of Agriculture.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physiol. Path. gén.	Journal de Physiologie et de Pathologie générale.
J. Phys. Radium	Journal de Physique et le Radium.
J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal.	Journal and Proceedings of the Asiatic Society of Bengal.
J. Proc. Roy. Soc. New South Wales	Journal and Proceedings of the Royal Society of New South Wales.

ABBREVIATED TITLE.	JOURNAL.
J. Roy. Agric. Soc. . . .	Journal of the Royal Agricultural Society.
J. Roy. Army Med. Corps . .	Journal of the Royal Army Medical Corps.
J. Roy. Hort. Soc. . . .	Journal of the Royal Horticultural Society.
J. Roy. Soc. West Australia	Journal of the Royal Society of West Australia.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Scot. Met. Soc. . . .	Journal of the Scottish Meteorological Society.
J. Soc. Arts . . . .	Journal of the Royal Society of Arts.
J.S.C.I. . . . .	Journal of the Society of Chemical Industry.
J. Soc. Dyers and Col. . .	Journal of the Society of Dyers and Colourists.
J. Soc. Leather Trades Chem.	Journal of the Society of Leather Trades Chemists.
J. Soc. Glass Tech. . . .	Journal of the Society of Glass Technology.
J. S. African Chem. Inst. .	Journal of the South African Chemical Institute.
J. Textile Inst. . . .	Journal of the Textile Institute.
J. Usines Gaz . . . .	Journal des Usines à Gaz.
J. Washington Acad. Sci. .	Journal of the Washington Academy of Science.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
K. Svenska Vet. Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Hand- lingar.
Kentucky Exp. Stat. Bull.	Kentucky Experimental Station, Bulletin.
Keram. Rundsch. . . .	Keramisch Rundschau.
Kew Bull. . . . .	Kew Bulletin.
Kōgyō-Kwagaku-Zasshi . .	Kōgyō-Kwagaku-Zasshi (Journal of Chemical Industry, Japan).
Kolloid Z. . . . .	Kolloid Zeitschrift.
Koll.-Chem. Beih. . . .	Kolloid-chemische Beihefte.
Kosmos . . . . .	Kosmos (Lemberg).
Kühn-Archiv . . . .	Kühn-Archiv.
Kunststoffe . . . .	Kunststoffe.
Lancet . . . . .	The Lancet.
Landw. Jahrb. . . . .	Landwirtschaftliche Jahrbücher.
Landw. Versuchs.-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Louisiana Bull. . . .	Louisiana Bulletin.
Louisiana Planter . . .	Louisiana Planter.
Lunds Univ. Årsskr. . .	Lunds Universitets Års-skrift.
Math. és Termés. Ert.	Mathematikai és Természettudományi Ertesítő, Buda- pest.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl. Vetenskapsakademiens Nobel- Institut.
Medd. on Grönland . . .	Meddelser on Grönland.
Med. Genees. Lab. Weltevreden	Mededeelingen uit het Geneeskundig Laboratorium te Weltevreden.
Med. Chron. . . . .	Medical Chronicle.
Med. Klinik . . . .	Medizinische Klinik.
Mem. Accad. Lincei . .	Memorie della Reale Accademia dei Lincei.
Mem. Accad. Sci. Torino .	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Kyōtō . .	Memoirs of the College of Science, Kyōtō Imperial University.
Mem. Coll. Sci. and Eng. Kyōtō	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Dept. Agric. India .	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mem. Soc. Ing. Civ. . .	Mémoires de la Société des Ingénieurs Civils de France.
Mem. Soc. Toscana Sci. Nat.	Memorie della Società Toscana di Scienze naturali residente in Pisa.
Mém. Poudres . . . .	Mémorial des Poudres.
Metall u. Erz . . . .	Metall und Erz.
Metallurgie . . . .	Metallurgie.

ABBREVIATED TITLE.	JOURNAL.
Metrop. Water Bd. Rep. . . . .	Metropolitan Water Board Reports.
Milch. Zentr. . . . .	Milchwirtschaftliches Zentralblatt.
Min. Mag. . . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
Mitt. Materialprüf. . . . .	Mittheilungen aus dem Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. med. Ges. Tokyo . . . . .	Mittheilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Naturforsch. Ges. Halle . . . . .	Mittheilungen der Naturforschenden Gesellschaft zu Halle.
Mitt. Path. Inst. K. Univ. Japan . . . . .	Mittheilungen aus dem pathologischen Institut der Kaiserlichen Universität zu Sendai, Japan.
Monatsh. . . . .	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Monatsh. Math. Physik . . . . .	Monatshefte für Mathematik und Physik.
Mon. Sci. . . . .	Moniteur Scientifique.
Month. Not. Roy. Astr. Soc. . . . .	Monthly Notices of the Royal Astronomical Society, London.
Münch. med. Woch. . . . .	Münchener medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen . . . . .	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Nature . . . . .	Nature.
Naturwiss. . . . .	Die Naturwissenschaften.
Naturw. Rdsch. . . . .	Naturwissenschaftliche Rundschau.
New York Agr. Expt. Sta. Bull. . . . .	New York Agricultural Experiment Station Bulletins.
New Zealand Dominion Laby. Rept. . . . .	New Zealand Dominion Laboratory Reports.
New Zealand J. Sci. Tech. . . . .	New Zealand Journal of Science and Technology.
Nippon Kwagaku Kwai Shi (J. Chem. Soc. Japan). . . . .	Nippon Kwagaku Kwa Shi (Journal of the Chemical Society of Japan).
Nova Acta Soc. Sci. . . . .	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nuovo Cim. . . . .	Il Nuovo Cimento.
Öfvers. Finska Vet.-Soc. . . . .	Öfversigt af Finska Vetenskaps-Societätens Förhandlingar, Helsingfors.
Oesterr. Chem.-Ztg. . . . .	Oesterreichische Chemiker-Zeitung.
Oversigt Danske Vid. Selsk. . . . .	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlingar.
Paper . . . . .	Paper.
Papierfabr. . . . .	Papier-Fabrikant.
Perf. and Essent. Oil Rec. . . . .	Perfumery and Essential Oil Record.
Per. spis. Sofia . . . . .	Periodicesko spisanie Sofia.
Petroleum . . . . .	Petroleum (German).
Pflüger's Archiv. . . . .	Archiv für die gesamte Physiologie des Menschen und der Thiere.
Pharm. J. . . . .	Pharmaceutical Journal.
Pharm. Weekblad . . . . .	Pharmaceutisch Weekblad.
Pharm. Zentr. . . . .	Pharmazeutische Zentralhalle.
Philippine J. Sci. . . . .	Philippine Journal of Science.
Phil. Mag. . . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans. . . . .	Philosophical Transactions of the Royal Society of London.
Phot. J. . . . .	Photographic Journal.
Phot. Korrr. . . . .	Photographische Korrespondenz.
Physica . . . . .	Physica.
Physical Rev. . . . .	Physical Review.
Physikal. Z. . . . .	Physikalische Zeitschrift.
Proc. Amer. Acad. Arts Sci. . . . .	Proceedings of the American Academy of Arts and Sciences.

ABBREVIATED TITLE.	JOURNAL.
Proc. Amer. Phil. Soc. .	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol. Soc. .	Proceedings of the American Physiological Society.
Proc. Amer. Soc. Biol. Chem.	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Civ. Eng.	Proceedings of the American Society of Civil Engineers.
Proc. Amer. Soc. Testing Materials	Proceedings of American Society for Testing Materials.
Proc. Austral. Inst. Min. Met.	Proceedings of the Australasian Institute of Mining and Metallurgy.
Proc. Camb. Phil. Soc. .	Proceedings of the Cambridge Philosophical Society.
Proc. Durham Phil. Soc. .	Proceedings of the Durham Philosophical Society.
Proc. Eng. Soc. W. Pa. .	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Inst. Civ. Eng. . .	Proceedings of the Institution of Civil Engineers.
Proc. Inst. Mech. Eng. .	Proceedings of the Institution of Mechanical Engineers.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci. .	Proceedings of the National Academy of Sciences.
Proc. Nova Scotia Inst. Sci.	Proceedings of the Nova Scotia Institute of Science.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc. . .	Proceedings of the Physical Society of London.
Proc. Physiol. Soc. . .	Proceedings of the Physiological Society.
Proc. Roy. Inst. . . .	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Irish Acad. .	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc. . . .	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin. .	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. Med. . .	Proceedings of the Royal Society of Medicine.
Proc. Roy. Soc. Queensland	Proceedings of the Royal Society of Queensland.
Proc. Roy. Soc. Tasmania .	Proceedings of the Royal Society of Tasmania.
Proc. Sci. Assoc., Vizianagram	Proceedings of the Science Association, Maharajah's College, Vizianagram.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Proc. U.S. Nat. Mus. . .	Proceedings of the United States National Museum.
Proc. verb. Soc. Toscana Sci. Nat.	Processi verbali Società Toscana di Scienze Naturali.
Pub. Fac. Sci. Univ. Masaryk.	Publications de la Faculté des Sciences de l'Université Masaryk (Spisy vydávané Přírodovědeckou Facultou Masarykovy University).
Pulp and Paper Mag. . .	Pulp and Paper Magazine of Canada.
Quart. J. Geol. Soc. . .	Quarterly Journal of the Geological Society.
Quart. J. Med. . . . .	Quarterly Journal of Medicine.
Radium in Biol. Heilkunde	Radium in Biologie und Heilkunde.
Rec. Australian Mus. . .	Records of the Australian Museum.
Rec. trav. bot. Néerland. .	Recueil des travaux botaniques Néerlandaises.
Rec. trav. chim. . . . .	Recueil des travaux chimiques des Pays-Bas.
Rend. Accad. Sci. Fis. Mat. Napoli .	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett.	Rendiconti dell' Reale Istituto Lombardo di Scienze e Lettere.
Rep. Aust. Assoc. Sci. . .	Report of the Australian Association for the Advancement of Science.
Rep. Brit. Assoc. . . .	Report of the British Association for the Advancement of Science.
Rev. chim. . . . .	Revue chimique . . . . . Oficijelni organ udruženja Jugoslavenskih Kemičara.
Rev. gén. Bot. . . . .	Revue générale de Botanique.
Rev. gén. Colloid. . . .	Revue générale des Colloïdes.
Rev. Gén. Mat. Col. . . .	Revue Générale des Matières Colorantes.

ABBREVIATED TITLE.	JOURNAL.
Rev. Mét. . . . .	Revue de Métallurgie.
Rev. Real Acad. Ciencias exact. Madrid	Revista de la Real Academia de Ciencias exactas, Físicas y Naturales de Madrid.
Riv. Min. Crist. Ital.	Rivista di Mineralogia e Cristallografia Italiana.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Sbornik Klubu Pri. .	Sbornik Klubu Přírodovědeckého (Prague).
Schweiz. Apoth. Ztg.	Schweizerische Apotheker Zeitung.
Schweiz. Chem.-Ztg. Science	Schweizerische Chemiker Zeitung. Science.
Sci. Ind. Rep. Roure-Bertrand Fils	Scientific and Industrial Reports of Roure-Bertrand Fils.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Rep. Tōhoku Imp. Univ.	Science Reports, Tōhoku Imperial University.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Seifensied. Ztg. . . .	Seifensieder Zeitung.
Sitzungsber. Akad. München	Sitzungsberichte der bayerischen Akademie der Wissenschaften zu München.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber. Ges. Naturwiss. Marburg	Sitzungsberichte der Gesellschaft zur Beförderung der gesammten Naturwissenschaften in Marburg.
Sitzungsber. Heidelberger Akad. Wis.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. Med. Naturwiss. Münster	Sitzungsberichte der Medizinisch-Naturwissenschaftlichen Gesellschaft zu Münster-in-Westfalens.
Sitzungsber. Naturforsch. Ges. Rostock	Sitzungsberichte der Naturforschenden Gesellschaft zu Rostock.
Sitzungsber. phys. med. Ges. Erlangen	Sitzungsberichte der physikalisch-medizinischen Gesellschaft zu Erlangen.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Skand. Arch. Physiol.	Skandinavisches Archiv für Physiologie.
Smithsonian Miscell. Coll. .	Smithsonian Miscellaneous Collections.
Soil Sci. . . . .	Soil Science.
South African J. Ind.	South African Journal of Industries.
South African J. Sci.	South African Journal of Science.
Sprechsaal. . . . .	Sprechsaal.
Stahl u. Eisen . . . .	Stahl und Eisen.
Staz. sper. agr. ital. . .	Stazioni sperimentali agrarie italiane.
Strahlenther . . . . .	Strahlentherapie.
Suom. Tied. Toim. . . .	Suomalaisen Tiedeakatemia Toimituksia.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Tech. Rep. Tōhoku Imp. Univ.	Technology Reports of the Tōhoku Imperial University, Sendai, Japan.
Tekn. Tidsk. . . . .	Teknisk Tidskrift.
Textilber. . . . .	Melliand's Textilberichte über Wissenschaft, Industrie und Handel.
Ther. Gegenw. . . . .	Die Therapie der Gegenwart.
Ther. Monatsh. . . . .	Therapeutische Half-Monatshefte.
Tonind.-Ztg. . . . .	Tonindustrie-Zeitung.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals .	Transactions of the American Institution of Metals.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.



ABBREVIATED TITLE.	JOURNAL.
Trans. Ceram. Soc. . . .	Transactions of the Ceramic Society.
Trans. Faraday Soc. . . .	Transactions of the Faraday Society.
Trans. Inst. Min. and Met.	Transactions of the Institution of Mining and Metallurgy.
Tr. N. Eng. Inst. Min. and Met.	Transactions of the North of England Institute of Mining and Metallurgy.
Trans. New Zealand Inst. .	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Roy. Irish Acad. . .	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada . .	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin. . .	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Soc. Sth. Africa	Transactions of the Royal Society of South Africa.
Tsch. Min. Mitt. . . . .	Tschermak's Mineralogische Mittheilungen.
U.S. Bureau of Mines, Bull. and Tech. Papers	United States Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau Plant Ind. . .	United States Bureau of Plant Industry.
U.S. Comm. Rept. . . . .	United States Commerce Reports, Daily Consular and Trade Reports.
U.S. Dept. Agric. Bull. . .	United States Department of Agriculture Bulletins.
U.S. Hyg. Labor. Bull. . .	United States Hygienic Laboratory Bulletins.
U.S. P. . . . .	United States Patent.
Univ. Illinois Bull. . . .	University of Illinois Bulletins.
Utah Agric. Coll. Exper. Stat. Bull. . . . .	Utah Agricultural College Experiment Station Bulletins.
Verh. Geol. Reichsanst. Wien	Verhandlungen der geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze	Verhandlungen der Gesellschaft deutscher Naturforscher und Aertze.
Verh. Naturhist. med. Ver. Heidelberg	Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg.
Verh. Naturhist. Rheinl. .	Verhandlungen des naturhistorischen Vereins der preussischen Rheinlande und Westfalens.
Verh. Physiol. Ges. Berlin	Verhandlungen der Physiologischen Gesellschaft zu Berlin.
Verh. Schweiz. Nat. Ges. .	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Basel.
Vict. Mem. Mus. Geol. Survey, Canada	Victoria Memorial Museum Geological Survey of Canada, Bulletin.
Videnskab. Skrifter . . .	Skrifter udgivne af Videnskabselskabet i Kristiania.
Wiener Klin. Woch. . . .	Wiener Klinische Wochenschrift.
Wiss. Abhandl. Physikal.-Tech. Reichsanst.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Wiss. Veröff. Siemens-Konz.	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Wochbl. Papierfabr. . . .	Wochenblatt für Papierfabrikation.
Woch. Brau. . . . .	Wochenschrift für Brauerei.
Yakugakuzasshi (J. Pharm. Soc. Japan).	Yakugakuzasshi (Journal of the Pharmaceutical Society of Japan).
Z. allg. Physiol. . . . .	Zeitschrift für allgemeine Physiologie.
Z. anal. Chem. . . . .	Zeitschrift für analytische Chemie.
Z. angew. Chem. . . . .	Zeitschrift für angewandte Chemie.
Z. anorg. Chem. . . . .	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol. . . . .	Zeitschrift für Biologie.
Z. deut. Geol. Ges. . . .	Zeitschrift der deutschen Geologischen Gesellschaft.
Z. deut. Oel-Fett Ind. . .	Zeitschrift der deutschen Oel- und Fett-Industrie.
Z. Elektrochem. . . . .	Zeitschrift für Elektrochemie.
Z. exp. Path. Ther. . . .	Zeitschrift für experimentelle Pathologie und Therapie.
Z. ges. Brauw. . . . .	Zeitschrift für das gesamte Brauwesen.

ABBREVIATED TITLE.	JOURNAL.
Z. ges. exp. Med.	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
Z. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.
Z. Immunit.	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
Z. Instrument.	Zeitschrift für Instrumentenkunde.
Z. Kryst.	Zeitschrift für Kristallographie.
Z. Leder-Gerb.-Chem.	Zeitschrift für Leder- und Gerberei-Chemie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physikal. chem. Unterr.	Zeitschrift für den physikalischen und chemischen Unterricht.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. prakt. Geol.	Zeitschrift für praktische Geologie.
Z. Sauerstoff Stickstoff Ind.	Zeitschrift für Sauerstoff und Stickstoff Industrie.
Z. Spiritusind.	Zeitschrift für Spiritusindustrie.
Z. Unters. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Z. wiss. Mikrosk.	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
Z. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie.
Z. Zuckerind. Cechoslov.	Zeitschrift für Zuckerindustrie der Čechoslovakischen Republik.
Zellstoff u. Papier	Zellstoff und Papier.
Zentr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Zentr. Zuckerind.	Zentralblatt für Zuckerindustrie.

# PROCEEDINGS

## OF THE

# CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, January 15th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
Robert P. Douglas .....	May 2nd, 1912.	Nov. 24th, 1924.
Khasberao B. Jadhava .....	June 16th, 1887.	Oct. 6th, 1924.
Edmund G. Lamb .....	May 4th, 1893.	Jan. 3rd, 1925.
George Downing Liveing .....	Nov. 21st, 1853.	Dec. 26th, 1924.
James McAlley .....	June 15th, 1899.	Feb. 1924.
William Sharman .....	June 4th, 1874.	Dec. 21st, 1924.

The PRESIDENT announced :

(1) That the names of the Members of Council who retire at the Annual General Meeting on the 26th March, 1925, and who are ineligible for re-election to the same office until the lapse of one year, are as follows :

President :

Prof. W. P. Wynne.

Foreign Secretary :

Dr. A. W. Crossley.

Vice-Presidents who have filled the office of President :

Prof. H. B. Dixon, Prof. P. F. Frankland.

Vice-Presidents who have not filled the office of President :

Prof. E. C. C. Baly, Dr. J. T. Hewitt.

Ordinary Members of Council :

(a) Town Members :

Dr. C. Dorée, Dr. J. J. Fox, Prof. J. R. Partington.

(b) Country Members :

Prof. I. M. Heilbron, Prof. J. W. McBain, Dr. W. H. Mills.

The following vacant places fall due to be filled at the Annual General Meeting on March 26th, 1925, in accordance with the Bye-Laws :

President	...	...	...	...	...	One vacancy.
Secretaries	...	...	...	...	...	One vacancy.
Foreign Secretary	...	...	...	...	...	One vacancy.
Vice-Presidents who have filled the office of						

President	...	...	...	...	...	Three vacancies.
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(Note: the vacancy additional to the two prescribed by the Bye-Laws is caused by the death of Sir James Dobbie.)

Vice-Presidents who have not filled the office of President						...	...	...	...	...	Two vacancies.
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Ordinary Members of Council :

- |  |                 |
|--|-----------------|
| (a) Town Members ( <i>i.e.</i> , those living within a radius of 50 miles from Charing Cross)    | Five vacancies. |
| (b) Country Members ( <i>i.e.</i> , those living beyond a radius of 50 miles from Charing Cross) | ...             |
| ...  | ...             |
| ...  | Two vacancies.  |

(Note: In accordance with the Bye-Laws, the number of vacancies in each of the categories (a) and (b) is three. But this year the vacancies among Town Members are increased by two and among Country Members reduced by two, owing to Prof. C. K. Ingold and Prof. J. Reilly, who are no longer resident in the London area, being transferred from Town to Country Members; while the resignation of a Country Member increases the number of vacancies among Country Members from one to two.

The Council has nominated :

Dr. A. W. Crossley to the office of President.

Dr. T. Slater Price to the office of Secretary.

Prof. F. G. Donnan to the office of Foreign Secretary.

(2) That the following address of congratulation was presented by Sir William Pope, F.R.S., to the Société Chimique de France on December 22nd, 1924, on the occasion of the celebrations of the 50th Anniversary of the foundation of Stereochemistry by van't Hoff and Le Bel in 1874 :

"To the Société Chimique de France.

"The President, Council and Fellows of the Chemical Society rejoice to learn that the Société Chimique de France is meeting on December 22nd on the occasion of the 50th anniversary of the foundation of Stereochemistry by Joseph Achille Le Bel and Jacobus Henricus van't Hoff.

"These two savants will ever be remembered for one of the most important advances in modern chemical thought and practice. The masterly conception which they gave to the chemical world has proved a fruitful incentive to brilliant researches, which have not only confirmed their theoretical reasoning, but have also immeasurably widened our knowledge of chemical structure.

"The Chemical Society, which is proud to have the name of Joseph Achille Le Bel on its list of Foreign Fellows, welcomes the opportunity of joining with its sister Society in doing honour to Le Bel and van't Hoff and in paying homage to their genius.

"Signed on behalf of the Chemical Society,

W. P. WYNNE, *President*.

JOCELYN THORPE, *Treasurer*.

T. SLATER PRICE, } *Secretaries*.

C. S. GIBSON, }

ARTHUR W. CROSSLEY, *Foreign Secretary*.

(L.S.)

"Sealed in Council this Eighteenth day of December, One Thousand Nine Hundred and Twenty-four."

The following were formally admitted Fellows of the Chemical Society: H. J. George, E. Rothstein, R. F. Goldstein, S. Barratt, E. Roberts, J. A. Aeschlimann, J. Ross, and C. I. Kelly.

Certificates were read for the first time in favour of:

Claud McClellan Bottomley, B.Sc., 43, Manor Road, Blackburn.

Frederick Stanley Brown, B.Sc., A.I.C., Rosebank, Tile Hill Lane, Coventry.

Herbert Isaac Coombs, B.Sc., B.A., Trinity College, Cambridge.

Ernest James Davis, 45, McClure Street, Ormeau Road, Belfast.

Henry Bell Footner, B.Sc., Great Dean, nr. Christchurch, Hants.

Robert Owen Griffith, M.Sc., A.I.C., Muspratt Laboratory of Physical Chemistry, The University, Liverpool.

Herbert Henry Hodgson, M.A., Ph.D., B.Sc., F.I.C., 130, Paley Road, Bradford.

Wilford Jordayne Johnson, Devanha, South Road, Brighton Beach, Victoria, Australia.

William Wenallt Jones, M.Sc., 19, White Hart Lane, Wood Green, N. 22.

Jacob Kracovski, B.Sc., 11, Ernest Street, E. 1.

John Joseph Laws, 45, Fulham Road, South Kensington, S.W. 7.

Alexander John Simpson Leiper, 74, Whitworth Road, South Norwood, S.E. 25.

William Hamilton McVicker, M.Sc., 45, Wellington Park, Belfast.

Frank Douglas Miles, Caldwell Road, West Kilbride, Ayrshire.

William Bayley Parker, F.I.C., 3, Murray Road, Rugby.

Isaac Vogel, B.Sc., 16, Wellclose Square, E. 1.

Nellie Walker, M.A., Ph.D., B.Sc., 15, Fintory Place, Broughty Ferry.

James Ewart Whipp, 15, St. John's Street, Longsight, Manchester.

The following papers were read:

"6-Chlorophenoxarsine." By E. E. TURNER and A. B. SHEPPARD.

- "The chemistry of the three-carbon system. Part III.  $\alpha\beta\gamma$ -Change in unsaturated acids." By G. A. R. KON and R. P. LINSTEAD.
- "The influence of valency direction on the dissociation constants of dibasic acids." By C. H. SPIERS and J. F. THORPE.
- "The relation of pilocarpidine to pilocarpine. Synthesis of 1:4- and 1:5-dimethylglyoxalines." By R. BURTLES, F. L. PYMAN, and J. ROYLANCE.

### LECTURE.

Sir William Hardy, Sec.R.S., will deliver his Lecture entitled "Problems presented by Films on Solid Surfaces," on Thursday, February 26th, 1925, at 8 p.m., in the Lecture Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W. 1.

### ANNIVERSARY DINNER.

The Anniversary Dinner will be held in the Grand Hall of the Hotel Victoria, Northumberland Avenue, W.C. 2, on Thursday, March 26th, 1925, the day of the Annual General Meeting. Further particulars will be issued shortly.

### ORDINARY SCIENTIFIC MEETINGS IN FEBRUARY.

February 5th, at 8 p.m.

February 19th, at 8 p.m., when a ballot for the election of Fellows will be held.

List of Papers received between December 19th, 1924, and January 15th, 1925. (This List does not include the titles of papers, or abstracts thereof, which have been read at a Scientific Meeting, or which have appeared in the Journal.)

- "Note on a simple constant-level apparatus for thermostats and water-baths." By J. M. SMITH.
- "Studies of equilibrium in systems of the type  $\text{Al}_2(\text{SO}_4)_3\text{-M''SO}_4\text{-H}_2\text{O}$ . Part I.  $\text{Al}_2(\text{SO}_4)_3\text{-CuSO}_4\text{-H}_2\text{O}$ .  $\text{Al}_2(\text{SO}_4)_3\text{-MnSO}_4\text{-H}_2\text{O}$  at 30°." By R. M. CAVEN and T. C. MITCHELL.
- "The mercuration of aromatic substances. Part I. Toluene." By S. COFFEY.
- "The chemistry of the three-carbon system. Part IV. A case of retarded mobility." By G. A. R. KON and R. P. LINSTEAD.

- "The velocity of reaction in mixed solvents. Part VIII. The velocity of formation of certain quaternary ammonium salts." By H. McCOMBIE, H. M. ROBERTS, and H. A. SCARBOROUGH.
- "Crystalline cuprous bromide." By D. B. BRIGGS.
- "Phenyl benzyl diketone and some derivatives." By T. MALKIN and R. ROBINSON.
- "Tautomerism of amidines. Part V. Methylation of glyoxalines by diazomethane. Bromination of 4(or 5)-phenylglyoxaline." By W. G. FORSYTH and F. L. PYMAN.
- "The mass of the hydrogen atom computed." By E. F. MORRIS.
- "The reduction of aromatic nitro-compounds." By R. W. WEST.
- "A redetermination of the atomic weight of boron." By H. V. A. BRISCOE and P. L. ROBINSON.
- "The interaction of nitrogen sulphide and sulphur. Nitrogen persulphide." By F. L. USHER.
- "The composition of the liquid and vapour phases in mixtures of glycerol and water." By M. P. I. V. IYER and F. L. USHER.
- "Note on some metallic couples decomposing water at the ordinary temperature." By E. S. HEDGES and J. E. MYERS.
- "Styrylbenzopyrylium salts. Part IV.  $\gamma$ -Styryl derivatives of 5:7-dihydroxy- and 5:7-dimethoxy-2-phenyl-4-methylbenzopyrylium chloride." By G. H. WALKER and I. M. HEILBRON.
- "Styrylbenzopyrylium salts. Part V. Distyryl derivatives of 7-hydroxy-2:4-dimethylbenzopyrylium chloride." By I. M. HEILBRON, G. H. WALKER, and J. S. BUCK.
- "Interactions of tellurium tetrachloride and acetic anhydride." By G. T. MORGAN and H. D. K. DREW.
- "Quantitative reduction by hydriodic acid of halogenated malonyl derivatives. Part IV. The influence of substitution in the amide group on the reactivity of the halogen atom in bromo-malonamide." By R. W. WEST.

CERTIFICATES OF CANDIDATES FOR ELECTION AT  
THE BALLOT TO BE HELD AT THE ORDINARY  
SCIENTIFIC MEETING ON THURSDAY, FEBRUARY  
19TH, 1925.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

ASHLEY, JULIUS NICHOLSON, 37, Scarsdale Road, Victoria Park, Manchester.  
British. Chemical Research student at the Victoria University of Manchester.  
B.Sc. Hons. (Birm.) 1923. A.I.C. 1923. (*Signed by*) Arthur Lapworth,  
R. Robinson, Frederick Challenger.

BARTRAM, GEORGE ALFRED, 19, Valley Rd., Spital, Chesterfield. British. Teacher of Chemistry. Student at University College, Nottingham, 1914-15, 1919 and 1920. B.Sc. (London Pass), 1920; B.Sc. (Lond., 2nd Class Hons. Chem.), 1922. Elected A.I.C. 1923. Teacher of Chemistry 1920 to present time. In charge of Chem. Advanced Course recognised by Board of Education 1922 to present time. (*Signed by*) F. Stanley Kipping, E. B. R. Prideaux, J. B. Firth, A. R. Blackburn.

BEEBY, GEORGE HARRY, 92, Ashby Rd., Loughborough. English. Chemistry Research Student. Training received at Loughborough College, under A. Bramley, Esq., D.Sc., F.I.C., etc. Hold degree of B.Sc. London. 2nd Hons. Chemistry. A.I.C. Diploma of Loughborough College (Hons.). Engaged on Metallurgical Research. (*Signed by*) Arthur Bramley, George Lawton, T. L. Garner, A. T. Eggington.

BISHOP, ARTHUR HENRY BURDICK, Westminster Training College, 130, Horseferry Rd., Westminster, S.W. 1. British. Assistant Lecturer in Chemistry. Research for one year at Jesus College, Oxford, on "Adsorption of Gases by Glass Wool." At present engaged in research on "Optical Rotatory Dispersion." (*Signed by*) P. C. Austin, E. E. Walker, Gerald Druce.

BLOOMER, VINCENT, B.Sc., 33, Balfour St., Oldham. British. Student. Have completed 3 years' Honours Chemistry Course at Victoria University, Manchester; am now doing one year's research course for the degree of M.Sc. (*Signed by*) Henry Stephen, F. P. Burt, D. H. Bangham.

BOTTOMLEY, CLAUD McCLELLAN, 43, Manor Road, Blackburn. British. Brewer. B.Sc. (Lond.) [Chemistry taken at Final Exam.]. (*Signed by*) W. J. Stansfield, A. Bramley, G. W. F. Holroyd.

BROWN, FREDERICK STANLEY, "Rosebank," Tile Hill Lane, Coventry. British. Research Student (in receipt of a Scientific and Industrial Research Grant). Two years' works experience. Academic training at University College of Wales, Aberystwyth, from 1919 up to present time. 1st Hons. B.Sc. (Wales). A.I.C. Over two years' research experience. *J.C.S.* 1923, Vol. 123, 2430. *J.C.S.* 1924, Vol. 125, 2219. (*Signed by*) T. Campbell James, C. R. Bury, Albert Green.

CHORLEY, PERCY, 87, Hazelbottom Rd., Crumpsall, Manchester. British. Chemist. M.Sc. (Vict.). Beyer Fellow, Victoria University, Manchester, 1914. Published, with Professor A. Lapworth, a paper on "A new series of nitrogenous compounds derived from camphoroxalic acid" (*Trans.*, 1920, 728). Chemist, on the staff of British Dyestuffs Corporation, Ltd. (*Signed by*) E. H. Rodd, R. Brightman, H. Swann, Carlton Butler, Morvan Lapworth.

COOMBS, HERBERT ISAAC, Trinity College, Cambridge. British. Student. Bachelor of Science, First-class Bachelor of Arts of Oxford; Research work under Professor Perkin, F.R.S., and Professor Hopkins, F.R.S. (*Signed by*) W. H. Perkin, H. Raymond Ing, R. H. Griffith, N. V. Sidgwick.

CORBET, ALEXANDER STEVEN, "Abbey Stone House," Sidmouth St., Reading. British. Chemist. B.Sc., Ph.D. (London University). A.I.C. Papers published with Professor H. Bassett: "The Hydrolysis of Potassium Ferricyanide and Potassium Cobalticyanide by Sulphuric Acid," *J.C.S.*, June 1924. "A Phase-rule Study of the Cupro-, Argento-, Auro-, and Thallo-cyanides of Potassium," August, 1924. (*Signed by*) H. Bassett, J. W. Dodgson, D. Roy Maxted.

CROWE, WILLIAM HAUGHTON, "Bettswville," Cherry Valley Park, Belfast (N. Ireland). British. Assistant in Chemistry (Q.U.B.). Research in Chemistry, Queen's University, Belfast. 1922-23, subject, "Effect of Light



on Brominations." 1923-24, University College, London, "Pyridones." (*Signed by*) A. W. Stewart, J. K. Marsh, H. Graham.

DAVIDSON, ALFRED, 91, Hazelbottom Rd., Cheetham, Manchester. British. Research Chemist, British Dyestuffs Corporation. B.Sc. (Glasgow) with distinction in Chemistry. T. S. Patterson and A. Davidson, *J.C.S.* (1912), 101, 374. (*Signed by*) E. J. Amies, C. Hollins, S. C. Bate.

DAVIS, ERNEST JAMES, 45, McClure Street, Ormeau Road, Belfast. British. Chief Assistant Chemist, Messrs. Harland and Wolff, Belfast. Ten years Industrial Chemist with Messrs. J. Stone & Co., Deptford; Martin's Heat Treating and Testing Works, Coventry; Harland and Wolff, Ltd., Belfast. (*Signed by*) Henry Wren, Theophilus Harper, James W. Porter.

DUFFIN, WALTER MARK, 35, Binfield Road, S.W. 4. English. Research Student. A.R.C.S. B.Sc., London. Engaged in Research. (*Signed by*) H. B. Baker, G. A. R. Kon, Arnold Stevenson, M. A. Whiteley.

DURRANT, ARTHUR HYNARD, 47, Cassiobury Rd., London, E. 17. British. Bacteriologist and Demonstrator in Chemistry, Guy's Hospital and The Technical Institute, E. 17. Inventor of a Constant Cell, see *Junior Mechanic*, May, 1921. (*Signed by*) W. H. Collier, H. L. Long, E. C. Edgar.

EATON, FREDERICK JOHN, Ph.D. (Edin.), B.Sc. (Edin.), A.I.C., Chemical Laboratory, Gas Light and Coke Coy., Horseferry Rd., Westminster. British. Research Chemist, Gas Light and Coke Coy. Formerly part time Assistant Dept. of Medical Chemistry, Univ. of Edinburgh, and Research Student under Prof. Barger, F.R.S., Univ. of Edinburgh. Paper on "Blue Adsorption Compounds of Iodine," accepted 9th Sept., 1924. (*Signed by*) George Barger, Ellen Field, John E. Mackenzie.

EDWARDS, GEORGE ALFRED, 21, Crystal Palace Rd., London, S.E. 22. British. Demonstrator in Chemistry, King's College, London University. B.A. Oxon., First Class Honours in Chemistry. B.Sc. Oxon. Demonstrator in Chemistry at King's College, London University. Joint author of "Amino-derivatives of Tetrahydrocarbazole." (*Signed by*) Samuel Smiles, A. J. Allmand, E. W. McClelland, Frank W. Stoyke.

EMELEUS, HARRY JULIUS, Battle, Sussex. British. Student. Research Student at Imperial College of Science and Technology. Graduate of London University. Chemistry (1st Class Hons.). A.R.C.S. (1st Class Chemistry). (*Signed by*) H. B. Baker, M. A. Whiteley, M. Carlton.

ESDALE, RALPH MARCRAVE, the Lytle Coal Co., Ltd., Minerville, Pa., U.S.A. British. Chemist to the Lytle Coal Co., Ltd., Minerville, Pa., U.S.A. Trained at Finsbury Technical College, 1919-1923. Desires to receive the publications of the Chemical Society. Awarded Diploma, July, 1922, A.C.G.F.C. (*Signed by*) A. J. Hale, H. M. Atkinson, R. J. Seal.

FLACK, EDWARD HUGH ST. CLAIR, 9, Bridge Street, Cambridge. British. born subject. Research Student in Organic Chemistry, Univ. of Cambridge. M.Sc. (Univ. of S. Africa). (*Signed by*) W. J. Pope, W. H. Mills, R. C. Odams.

FOOTNER, HENRY BELL, Great Dean, nr. Christchurch, Hants. British. Chemist. B.Sc. (Lond.), 1st Hons. Chemistry. 1922-1924, Research work on reactions of Alkyl Thiosulphates and Allied Compounds—publication pending. (*Signed by*) Samuel Smiles, C. Montague Bere, Hubert Painter.

GEOGHEGAN, DESMOND, 13, Port View, Heavitree, Exeter. British. Analytical Chemist. Three years pupil-assistant to T. Tickle, Esq., Devon County Analyst; two and a half years' experience in Practical Organic Chemistry and General Chemical Analysis at University College, Exeter, under Prof. W. H. Lewis. Educated at Sherborne School, Dorset, and at Douai School, Berks. Desires Fellowship, to have use of the Library, and

to keep in touch with modern research through the publications of the Society. (*Signed by*) Thomas Tickle, S. Glasstone, F. Southerden, R. King, W. H. Lewis.

GIBBY, CLIFTON WILLIAM, "The Rise," Foxley Lane, Purley, Surrey. British. Research Worker in Chemistry. Three years' study of Chemistry at University College, London, including a year's research with Professor Irvine Masson. Honours B.Sc. in Chemistry. A.I.C. by Exam. Now appointed Research Assistant to Mr. A. C. Egerton, at the Clarendon Laboratory, Oxford. (*Signed by*) F. G. Donnan, Henry Terrey, L. F. Gilbert.

GIBSON, REGINALD OSWALD, 41, Peak Hill, Sydenham, S.E. 26. British. Research Chemist. Bachelor of Science (London), 1924. Associate of the Institute of Chemistry, 1924. (*Signed by*) F. G. Donnan, W. E. Garner, O. L. Brady, I. E. Weber, V. W. Slater.

GLIMMINGHAM, CONRAD THEODORE (F.I.C.), Haddon House, Aarenbury Lane, Harpenden, Herts. British. Research Chemist, Insecticides and Fungicides Dept., Rothamsted Experimental Station, Harpenden, Herts. Research and Advisory Work in Agric. Chemistry at University of Bristol, 1909-1919. Research Work, Chemical Warfare Dept., 1916-1919. Chemist, Research Dept., Olympia Agric. Co., 1920-1923. Since then at Rothamsted Experimental Station. Various papers on Agric. Chem. subjects in *Jour. Agric. Sci.*, *Ann. App. Biol.*, etc. (*Signed by*) E. J. Russell, H. J. Page, H. W. Dudley.

GOODSPEED, JONATHAN, 36, Vicarage Lane, East Ham, E. 6. Student. Chemistry Student at East London College. (*Signed by*) J. R. Partington, E. E. Turner, B. D. Shaw.

GREENHALGH, RICHARD, 139, Stuart Street, Clayton, Manchester. British. Research work at Manchester University for M.Sc. Degree. Degree of B.Sc. in Chemistry Honours at Manchester University, Class II, Division I. (*Signed by*) Arthur Lapworth, Henry Stephen, Frederick Challenger, Fred Fairbrother, Colin Campbell.

GRIFFITH, ROBERT OWEN, Muspratt Laboratory of Physical Chemistry, Liverpool University. British. Lecturer in Physical Chemistry, Liverpool University. B.Sc., 1st Class Hons. Chem. (Liverpool), 1914; M.Sc., 1915; A.I.C., 1915-1918. Chemist under D.I.H.E., Liverpool. 1919, Lecturer in Physical Chemistry, Liverpool University. *Publications*: "Einstein's Law of the Photochemical Equivalent," Appendix VII. Lewis's "System of Physical Chemistry," Vol. 3, 3rd edition. Sections "Chemical Equilibrium" and "Reaction Velocity" in "Tables Annuelles de Constantes," Vol. 5 (in print). Papers in *J.C.S.*: (1) 1916, 109, 67; (2) 1917, 111, 389; (3) 1921, 119, 1948; (4) 1923, 123, 2752; (5) 1923, 123, 2767. Also *Trans. Faraday Soc.*, 1921, 17, 525. (*Signed by*) W. C. M. Lewis, F. C. Guthrie, E. C. C. Baly, I. M. Heilbron.

HAILWOOD, ANTHONY JAMES, Hazel Bank, Hazel Road, Altrincham. British. Research Chemist in the British Dyestuffs Corporation, Ltd., Manchester. Formerly on the manufacturing staff of the same Corporation. B.Sc. with 1st Class Honours in Physics (Manchester University). (*Signed by*) W. H. Perkin, G. R. Clemo, S. C. Bate.

HISCOCKS, EDWARD STANLEY, 5, Rosehill, Swansea. British. Research Student, Chemistry Dept., University College, Swansea. Part-time Lecturer in Chemistry to the Municipal Technical College, Swansea. Hons. Graduate (Wales) in Chemistry. Part-time Lecturer in Physical and Inorganic Chemistry to the Municipal Technical College, Swansea. (*Signed by*) J. E. Coates, Leonard E. Hinkel, Ernest E. Ayling.

HODGSON, HERBERT HENRY, M.A. (Cambridge), B.Sc. (London), Ph.D. (Heidelberg), F.I.C., 136, Paley Road, Bradford. British. Head of Colour Chemistry Dept., Technical College, Huddersfield, since Sept. 1918. Previous posts, 1908-1912, Lecturer and Research Chemist, Technical College, Bradford; 1912-1915, Head of Chemical Dept., Northern Polytechnic Institute, London, N.; 1915-1918, Chief Chemist to Messrs. Brotherton & Co. at Birmingham and Stourton (Leeds). *Papers*: (1) "Dissertation," Heidelberg, 1908; (2) "Some Reactions of Phenyl Iodide, Chloride, and Iodosobenzenes Acetate," *Proc. Camb. Phil. Soc.*, 1908; (3) "Isomere organische Magnesiumverbindungen" (with J. Schmidlin), *Ber.*, **41**, 430-437; (4) "Triphenylelessigsäure und Tritolylessigsäure" (with J. Schmidlin), *Ber.*, **41**, 438-447; (5) "The Iodination of Phenols, etc." (with W. M. Gardner), *J.C.S.*, 1909, **95**, 1819-1827; (6) "The Development of Sulphuric Acid from Sulphide Dyestuffs and from Free Sulphur" (with W. M. Gardner), *J. Soc. Chem. Ind.*, 1910; (7) "The Action of Sulphur on Amines. Part I. *o*-Toluidine," *J.C.S.*, 1912, **101**, 1693-1701; (8) "The Action of Sulphur on Amines. Part II. Aniline," *J.C.S.*, 1914, **105**, 952-956; (9) "Nitrosation of Phenols. Part I. 3-Chloro-4-nitrosophenol and its Conversion into Two Isomeric Chloroquinone Monoximes" (with F. H. Moore), *J.C.S.*, 1923, **123**, 2499-2507; (10) "The Preparation of 2- and 4-Nitro-1-naphthols" (with E. Kilner), *J.C.S.*, 1924, **125**, 808-811; (11) "Direct Sulphuration of Aniline," *J.C.S.*, 1924, **125**, 1855-1858; (12) "Mononitration of *p*-Chlorotoluene" (with P. Anderson), *J.C.S.*, Oct. Notes, 1924; 4 papers now before the Publication Committee. *Patents*: Some New Sulphur Compounds and Dyestuffs therefrom, 1912; Preparation of Meta Halogenated Phenols, Brit. Pat. 200714; Preparation of Dihalogenated Fluoranes, Brit. Pat. 205254; Preparation of Tautomers of Nitroso-*m*-halogenated Phenols, Brit. Pat. 206734; 2 now filing on *m*-Hydroxybenzaldehyde and Azo Dyestuffs from Alkyl Thiol Amines. (*Signed by*) James Bruce, L. Gordon Paul, R. W. Merriman.

HUGHES, DAVID, 18, Holmes Grove, Westbury on Trym, Bristol. British. Chemist. At present on the Staff of British Colloids, Ltd. Passed Qualifying Examination of the Pharmaceutical Society, 1894. Engaged for 10 years in Chemical and Clinical Laboratory Work on my own account in Bath and Clifton. Studied Bacteriology under Prof. Stanley Kent, Bristol University. Co-operated with Dr. A. L. Flemming, Bristol, in a monograph on the Spectroscopic Examination of Blood in Ethyl Chloride Anaesthesia. Desirous of keeping up to date in developments of Chemical Science and to be allowed the privilege of the Library. (*Signed by*) John Macvie Hill, Archibald Macpherson, John F. Ward, Geo. A. Turner.

HUGHES, KATHLEEN HARRIET, 8, Ormiston Drive, Knock, Belfast. British. Lecturer in Pure and Applied Chemistry, Municipal College of Technology, Belfast. Lecturer in Chemistry, M.C.T.B., 1920-1924. Temporary Assistant Chemist, Government Laboratory, Strand, 1917-1920. (*Signed by*) Henry Wren, Theophilus Harper, James W. Porter.

HUNT, ARTHUR FREDERICK, 6, Seabrooke Cottages, Front Lane, Cranham (nr. Upminster), Essex. Chemical Research Student. B.Sc. (Lond.), 1st Class Hons. Research Student at East London College under Dr. E. E. Turner. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones, E. E. Turner.

INGHAM, BERTRAM HOBART, Yew Bank, Langham Rd., Bowdon, Cheshire. British. Research Student. B.Sc. Hons., Victoria University, Manchester (*Signed by*) Arthur Lapworth, F. P. Burt, J. E. Myers, Henry Stephen, R. Robinson.

JOHNSON, JOHN DOBNEY, 6, Edward St., Loughborough, Leics. British. Research Student. B.Sc. Hons., London. Royal Scholar. Research Student. (*Signed by*) Jocelyn Thorpe, M. A. Whiteley, G. A. R. Kon, Arnold Stevenson.

JOHNSON, WILFORD JORDAYNE, "Devanha," South Rd., Brighton Beach, Victoria. Licensed Gold Assayer and Chemical Analyst. Associate, Australian Chemical Institute. 1913-1922 (except for War Service), Assistant to Mr. Henry W. Levy, Assayer and Metallurgical Chemist, Melbourne, Australia. September 1922 to date, in partnership with Mr. Henry W. Levy, in private practice as Assayers and Metallurgical Chemists. (*Signed by*) D. O. Shiels, Henry W. Levy, Robert Law.

JONES, CECIL BRELLISFORD OAKES, Old Sewage Works, Whitley, Coventry. British. Analytical Chemist to the Coventry City Council. Four years assistant to W. D. Scouller, Esq., M.Sc., A.I.C., F.C.S. Ten years chief assistant to John Haworth, Esq., F.I.C., F.C.S. Author of "Sewage Works Analyses" (*Surveyor*, April 25th, 1924). (*Signed by*) John Haworth, W. D. Scouller, James H. Kershaw.

JONES, WILLIAM WENALIT, 19, White Hart Lane, Wood Green, N. 22. British. Assist. Chemist, The British Drug Houses, Ltd., Graham St., City Road, N. 1. B.Sc. Wales, June 1922; 2nd Class Honours Chemistry. M.Sc. Wales, June 1924. One session's Research Experience at the University College of North Wales, Bangor. (*Signed by*) Francis H. Carr, Charles Alex. Hill, S. Sugden.

KENNEDY, ALAN RICHMOND, 88, Sellons Avenue, Harlesden, N.W. 10. British. Assistant Chemist (Thomas de la Rue & Co., 110, Bunhill Row, E.C.). Undergraduate (University of London) in Faculty of Science (graduation, 1925). Employed in commercial Laboratory (founded by Dr. Hugo Müller). Desirous of receiving Society's literature concerning particularly modern researches in Organic Chemistry. (*Signed by*) Hubert L. Lucking, P. C. L. Thorne, E. de Barry Barnett, Henry J. S. Sand.

KENYON, FRANK, Power Station, Creekmouth, Barking, Essex. British. Chemist to the New Electrical Station, Barking, County of London Electric Supply Co., Ltd. Associate of the Institute of Chemistry, Branch D. (*Signed by*) J. Kenyon, J. L. White, Harold Hunter.

KING, FREDERICK ERNEST, 101, Cavendish Road, Highams Park, Essex. British. Student (Research at East London College). (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones.

KNOTT, ERIC, 21, West Richmond St., Edinburgh. British. Lecturer in Chemistry and Physics at the Royal Dispensary and School of Pharmacy of Edinburgh. Student of the Royal Dispensary and School of Pharmacy of Edinburgh, 1919-21, from which place I obtained the Qualifying Certificate of the Pharmaceutical Society and also the Diploma of Pharmaceutical Chemist. For past three years engaged as Lecturer at above School in Chemistry and Physics. (*Signed by*) Russell G. Thin, A. Scott Dodd, William Duncan.

KRACOVSKI, JACOB, 11, Ernest St., London, E. 1. English. Research Student. B.Sc., 1st Class Hons. in Chemistry. At present engaged in research. (*Signed by*) Jocelyn Thorpe, G. A. R. Kon, M. A. Whiteley, E. H. Farmer.

LAMBOURNE, HERBERT, 44, Brighton Road, S. Croydon, Surrey. British. Head of the Chemistry Dept., Borough Polytechnic Institute, Borough Road, S.E. 1. Late Senior Lecturer in Organic Chemistry, University College, Nottingham. Research work on "Quinaldine and Derivatives," "Methyl-

stannonic Acid and Derivatives." M.A. (Cantab.), M.Sc. (Lond.), F.I.C. (*Signed by*) F. S. Kipping, J. B. Firth, E. B. R. Prideaux, F. C. Laxton.

LAW, JOHN JOSEPH, 45, Fulham Rd., South Kensington. English. Chemist, Dentist, and Optician. Holding the Qualifying Certificate of the Pharmaceutical Society of G.B. (Lond.). Hon. Treasurer of the Chemists' Dental Society of Great Britain and Ireland (Reg. No. 15073). Hon. Gen. Secretary of the Institute of Chemists and Opticians. Examiner in Refraction to the Institute of Chemists and Opticians. Member of the Public Dental Services. At one time principal of the West End College of Chemistry and Pharmacy. Private tutor of Chemistry for many years. (*Signed by*) Percy Barrs, Robert W. Lindsey, James Harry Smith, Frank B. Arnold.

LE FEVRE, RAYMOND JAMES WOOD, 17, Broadway Avenue, St. Margarets, Twickenham, Md. British. University Undergraduate. Chemistry Student, East London College (2nd year of final). (*Signed by*) J. R. Partington, E. E. Turner, B. D. Shaw.

LEIPER, ALEXANDER JOHN SIMPSON, 74, Whitworth Road, South Norwood, London, S.E. 25. Scottish. Chemist. I wish to join the Chemical Society in order to keep in touch with up-to-date research and proceedings. I am an Associate of the Royal College of Science in Chemistry. (*Signed by*) M. A. Whiteley, Jocelyn Thorpe, James C. Philip.

LENNANE, ALFRED JAMES ANDREW, 22, Ryder St., St. James's, S.W. 1. British. Physician and Surgeon. Formerly Opium Analyst to the Indian Government. M.R.C.S., L.R.C.P. (*Signed by*) Frank Radcliffe, Thos. R. Owles, Samuel Gray Fenton.

LILEY, FREDERICK WILLIAM, 41, Beaconsfield Rd., West Croydon. British. Assistant, Croydon Borough Analyst. Student at King's College, London. 2 Years assistant to Croydon Borough Analyst. (*Signed by*) Lester Reed, Eric K. Rideal, Ed. Hinks.

LUNT, JAMES GILBERT, 17, York Avenue, Sefton Park, Liverpool. British. B.Sc. of Liverpool. Chemical Analysis, c/o Anglo-South American Meat Co., San Martin 235, Buenos Aires, Argentina. (*Signed by*) I. M. Heilbron, William Doran, Stanley J. C. Snedker.

McVICKER, WILLIAM HAMILTON, 45, Wellington Park, Belfast. British. Chemical Research Student. B.Sc. (1st Class Honours), and M.Sc., Queen's University of Belfast. Musgrave Research Student, Queen's University of Belfast, 1923-25. Joint author of 7 papers as follows: *J.C.S.*, 123, 642, 817, 820, 2147; 125, 1743; *J. Amer. C. S.*, XLVI, 1351; *Phil. Mag.*, XLVIII, 628. (*Signed by*) A. Killen Macbeth, Ernest W. McClelland, A. W. Stewart, J. K. Marsh, H. Graham.

MANN, THOMAS, Alexander Terrace, Bransty, Whitehaven. British. Partner in firm of Hellon and Mann, Analytical and Consulting Chemists, Whitehaven. (*Signed by*) G. W. Martin, C. A. Mitchell, Bernard Dyer.

MASCARENHAS, VINCENT MARK, Bangalore. Indian Christian. Student, Indian Institute of Science, Bangalore. Bachelor of Arts of the University of Mysore with Chemistry as a main subject. Completed the work on the Chemistry of Indian Black Mustard Seed Oil, and that of Malabar Tallow (*Vateria Indica*) awaiting publication in the Journal of the Indian Institute of Science. (*Signed by*) J. J. Sudborough, M. O. Forster, Roland V. Norris.

MILES, FRANK DOUGLAS, Caldwell Road, West Kilbride, Ayrshire. English. Research Chemist. Asst. Lecturer in Inorganic Chemistry, Heriot-Watt College, Edinburgh, 1909-1915. Service in Dept. of Explosives Supply,

1915-1919. Senior Research Chemist, H.M. Factory, Gretna. Chief Research Chemist, Messrs. Burt, Boulton, and Haywood, 1919-1922. At present a member of the Research Section of Nobel Industries, Ltd. *Publications*: "Egyptian Blue," with H. P. Laurie and W. F. P. McLintock, *Proc. Roy. Soc.*, 1914. Also papers in *Proc. Roy. Soc. Edin.* (two, 1915), and in *Journ. Soc. Chem. Ind.*, 1920 and 1922. "A Volumetric Method for the Estimation of Lead," *J.C.S.*, 1915, **107**, 988; "The Solubility of Sulphur Dioxide in Sulphuric Acids" (with J. Fenton), *J.C.S.*, 1920, **117**, 59. Also author of forthcoming volume of Lunge's "Sulphuric Acid and Alkali" entitled, "Sulphuric Acid—Contact Process." (*Signed by*) John Weir, Norman Picton, W. Young.

NIGHTINGALE, EDWARD ARTHUR, 39, Pacific Rd., Fords Park Rd., Canning Town, E. 16. British. Commercial Analytical Chemist, Messrs. Burt, Boulton, and Heywood, Ltd., Coal Tar and Creosote Works, Silvertown, 1918-1920. Messrs. Pinchin, Johnson & Co., Paint and Varnish Manufacturers, Silvertown, 1920. Student at Borough Polytechnic for Paints, Oils, and Colours. Student at East Ham Technical College, Chemistry, 6 years' course. City and Guilds of London Institute, Coal Tar, 1st Class certificate. (*Signed by*) R. W. Griffiths, W. H. Barker, W. T. Clough.

OFFORD, FREDERICK WILLIAM, 66, Watford Road, Canning Town, London, E. 16. English. Analytical Chemist. National Certificate in Chemistry, "Higher" or "Advanced," 1923. Worked under J. Bendix, F.I.C., F.C.S. (1915-1920). (*Signed by*) E. W. Griffiths, E. G. Churchill, W. H. Barker.

OUTRIDGE, LIONEL EDWARD, "Fernhurst," The Avenue, Chingford, Essex. British. Research Student. B.Sc. (London), Honours Chemistry. Research student at East London College under Dr. D. C. Jones. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones, E. E. Turner.

PARKER, THOMAS WEBSTER, Mildenhall, Suffolk. British. Chemist. Student at the Royal College of Science (London), 1919-23. A.R.C.S., 1921. Chemist to the Dartmoor China Clay Co. (*Signed by*) James C. Philip, M. B. Donald, A. B. P. Page.

PARKER, WILLIAM BAYLEY, F.I.C., 3, Murray Road, Rugby, Warwickshire. Chief Chemist (Research and Works), The British Thomson-Houston Co., Ltd., Rugby. Chief Chemist to B.T.H. from April 1902, and Author of "Specifications for Foundry Pig Irons," Pt. I and II., Proceedings British Foundrymen's Association, 1912-13 and 1906; "Specifications for Alloys for High Speed Superheated Steam Turbine Blading," *Jnl. Inst. of Metals*, No. 2, 1915; "Purchasing Specifications for Resins and Shellac," *Jnl. Oil and Colour Chemists' Association*, Vol. V, 1922; "Variation of Refractive Index and Density of Benzene with Temperature," W. B. Parker and G. Thompson, *Trans. Chem. Soc.*, 1922, Vol. **121**. (*Signed by*) Percy F. Frankland, S. Judd Lewis, Gartha Thompson.

PARSONS, STUART RUSSELL, 65, Oakfield Road, Ilford. Research Student (Chemistry). B.Sc. (Lond.), Honours Chemistry. A.I.C. Research student at East London College, under Dr. E. E. Turner. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones, E. E. Turner.

PAYNE, WILLIAM SAMUEL, Moseley House, Rounds Green, Oldbury. English. Chemist. 5 years Laboratory Steward, Oldbury Secondary Schools. 3 years Laboratory Steward, Oldbury Technical Schools. 2 years Demonstrator and Assistant Chemistry Master, Oldbury Technical Schools. U.E.I. Certificate in Advanced Inorganic and Physical Chemistry, 1924. (*Signed by*) John G. Clarke, C. Mansfield Swain, E. Pritchett.

PIERSON, KENNETH JOHN, 105, Winterbourne Road, Thornton Heath.

British. Two years Assistant to the Croydon Borough Analyst. (*Signed by*) Lester Reed, Ed. Hinks, Henry P. Stevens.

PIKE, RICHARD EDWIN, 6, Haymarket, London, S.W. 1. British. Student. Pass B.Sc. (Lond.). Studying for Honours at Royal College of Science since October, 1923. (*Signed by*) H. B. Baker, H. F. Harwood, M. A. Whiteley, James C. Philip.

PLUMBRIDGE, DOUGLAS VICTOR, 21, Heathfield Rd., Wavertree, Liverpool. British. Research Chemist. Ph.D. (Munich). A.R.C.Sc. (London). A.I.C. On the staff of the Chemical Dept., Messrs. The Salt Union, Ltd., Western Point, Cheshire. (*Signed by*) A. Bramley, Norman M. Comber, James C. Philip.

PRESTON, JOHN MASSEY, The Dower House, Euxton, Chorley, Lancs. British. Private Research in Chemistry. B.Sc., 2nd Class Hons. Chem. (Liv.). A.I.C. (*Signed by*) E. C. C. Baly, H. Rogerson, F. C. Guthrie.

RAPER, RICHARD, 12, Mill Lane, Cambridge. British. Research Student. 1st Class Honours in Nat. Sci. Tripos, Parts I and II (Chemistry) of Cambridge University. Two years' research work under Dr. Mills, F.R.S., and two years' experience as Demonstrator in Cambridge University Chemical Laboratory. (*Signed by*) W. J. Pope, W. H. Mills, H. R. Stevens.

RULE, JOHN FREDERICK JAMES, 29, Alexandra Road, East Ham, E. 6. Research Student. Have passed the B.Sc. Hons. examination in Chemistry of London University, and I am undertaking Research Work under Professor Partington. (*Signed by*) J. R. Partington, W. H. Patterson, E. E. Turner.

SCORAH, LESLIE VIVIAN DONALD, 139, Dodworth Road, Barnsley (Yorks). British. Research Student. B.Sc. (Hons. Chem.) Sheffield. A.I.C. (*Signed by*) W. P. Wynne, G. M. Bennett, F. G. Tryhorn, Arthur W. Chapman.

SHEPPARD, GEORGE FREDERICK, 72, Mortlake Rd., Kew Gardens, Surrey. British. Chemist, Cl. II. Department of Government Chemist. Position as above. Student, Royal College of Science, London, 1900-2, passed examinations of the Associateship Course in Chemistry for Revenue Students. Past experience: Analytical work in above Department since November, 1902. (*Signed by*) Thos. J. Cheater, W. Williamson, Robert Robertson, Geo. Stubbs.

SHEVLIN, JOSEPH THOMAS, "Corwen," Frederick Road, Wylde Green, Birmingham. British. Patent Agent. Associate of the Chartered Institute of Patent Agents. Associate of the Institute of Physics. Associate of the Institution of Electrical Engineers. Fellow Physical Society of London. I am desirous of becoming a Fellow of the Society in order that I may be well versed in the more recent developments in Chemistry. (*Signed by*) G. G. Henderson, F. J. Wilson, E. W. Moss.

SMETHURST, ARTHUR FREDERICK, Nippon, Cedar Road, Sutton, Surrey. British. Undergraduate. Student in Chemistry at the Royal College of Science since October, 1922. (*Signed by*) H. B. Baker, H. F. Harwood, M. A. Whiteley, James C. Philip.

SMEWING, ETHEL MINNIE, 42, Park Avenue South, Crouch End, N. 8. British. Teacher. B.Sc. Hons. Chem. (Lond.). Teacher of Chemistry. (*Signed by*) J. F. Spencer, M. S. Crewdson, H. Crompton.

SMITH, ALTON EWART CLARENCE, Breydon, Oakmount Avenue, Southampton. British. Lecturer in Physical Chemistry, University College of Southampton. Lecturer as above since 1919. (*Signed by*) D. R. Boyd, C. K. Ingold, C. F. Cross.

SNELUS, SUZANNE MABEL LAVINIA, 67, Elgin Mansions, W. 9. British. Analytical and Consulting Chemist. Member of the Pharmaceutical Society

Associate of the Institute of Chemistry. Senior Analyst to Messrs. Parke Davis & Co. Chemist in Charge to Messrs. J. C. Arnfield & Sons. Assistant Research worker, Dr. F. W. Passmore. (*Signed by*) P. C. L. Thorne, E. de Barry Barnett, Henry J. S. Sand.

SPIERS, CLAUDE HYMAN, 34, Brondesbury Road, N.W.6. British. Research Chemist. M.A. (Cambridge). B.Sc. (London). Ph.D. (Cambridge). *T.*, 1924, 125, 450. (*Signed by*) Jocelyn Thorpe, Arnold Stevenson, G. A. R. Kon, H. M. Spiers.

STERN, HAROLD JACOB, 17, Croxteth Grove, Sefton Park, Liverpool. British. Chemist to firm of paper stainers. Research on Photosynthesis, Liverpool University, 1921-22. Research in Organic Chemistry under Prof. W. H. Perkin, Oxford, 1922-24. B.Sc. (Hons. Chem.), Liv., 1921. Ph.D., Liv., 1923. B.Sc., Oxon., 1924. Baly, Heilbron, and Stern, 1923, 123, 185. (*Signed by*) W. H. Perkin, Fredk. A. Mason, G. R. Clemo, S. G. P. Plant, E. Hope, F. Raymond Ing.

STILL, CHARLES JAMES, 50, Queen's Parade, Bangor, Co. Down. British. Lecturer in Bleaching and Dyeing, Municipal College of Technology, Belfast. B.Sc. (Lond.); M.Sc. and Ph.D. (Queen's Univ., Belfast). Joint author of several communications (in collaboration with Dr. Henry Wren) on Diphenylsuccinic Acids, published in *J. Chem. Soc.* (*Signed by*) Henry Wren, James W. Porter, Theophilus Harper.

SYED, MOHAMMAD HASSAN, Rupar (Amballa), India. Indian Muhammadan. Demonstrator, MacLagan Engineering College, Lahore, India. B.Sc. (Chemistry), Punjab University. Desirous of being in touch with the recent work in Chemistry. (*Signed by*) S. D. Muzaffar, S. J. Kohli, Edwin Theodore Dean.

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TIMMS, ERIC SPENCER, 96, Grange Park Rd., Thornton Heath. Research Student (Chemistry). B.Sc. (London), Honours Chemistry. Research Student at East London College under Dr. D. C. Jones. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones, E. E. Turner.

TITTERINGTON, ERIC, Abdine Palace, Cairo, Egypt. British. Private Chemist to H.M. the King of Egypt. Member of the Pharmaceutical Society of Great Britain. Engaged in the examination of food and all drugs used in the household of His Majesty. Attached to the Medical Staff of His Majesty for Physiological work. Appointed Examiner in Chemistry to the Cairo Medical School, 1924. (*Signed by*) Ayerst Henham Hooker, W. Morris Colles, C. S. Gibson.

TUDHOPE, THOMAS MARTIN AITKEN, 8, Anson Road, Tufnell Park, London, N. 7. British. Temporary Assistant Chemist in the Government Laboratory. B.Sc. (St. Andrews), with Special Distinction in Chemistry. Ph.D. (St. Andrews). Carnegie Research Scholar for two years (sessions 1921-1923). Engaged in Chemical Research at University College, Dundee, for three years. "Optically Active  $\beta$ -Phthalimino- $\beta$ -phenylpropionophenones," McKenzie and Tudhope, *J.C.S.*, 1924, 125, 923. (*Signed by*) Robert Robertson, Geo. Stubbs, J. J. Fox.

VASS, CHARLES CYRIL NORREY, "Holmleigh," Harboro' Rd., Kingsthorpe, Northampton. British. Student. B.Sc. Ordinary (Leeds, 1924). (*Signed by*) C. K. Ingold, P. K. Dutt, W. A. Wightman, H. M. Dawson, R. Whytlaw-Gray.



VILLAGE, JOHN HARRY, 61, Broxholme Lane, Doncaster. British. Chemist. B.Sc. Hons. (Lond.). For 5 years engaged as Assistant Chemist by the Koppers' Coke Oven Co. under G. E. Foxwell, M.Sc., A.Inst.P., F.C.S. Here I have assisted in numerous researches on coal and its by-products. Now in charge of Laboratory. (*Signed by*) G. E. Foxwell, P. G. Mander, G. D. Crosley.

VOGEL, ISRAEL, 16, Wellclose Square, London, E. 1. Research Student in Chemistry at the East London College. B.Sc., 1st Class Honours Chemistry. Neil Arnott Scholar and Bronze Medallist in Chemistry of the University of London. Author of "The Constitution of the Thionic Acids," *Chem. News*, 128, 325-327, 342-345, 361 (1924). (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones.

WILSON, JOHN, 115, Canterbury Rd., North Harrow. British. Student engaged in Biochemical Research, Imperial College of Science and Technology, M.Sc. (Sheffield). (*Signed by*) S. B. Schryver, Harold Mastin, J. Knaggs.

WALKER, NELLIE, 15, Fintry Place, Broughty Ferry, Forfarshire. Lecturer in Chemistry, University College, Dundee (University of St. Andrews). M.A., B.Sc., Ph.D. (St. Andrews). Conjoint author of the following papers in the Journal of the Chemical Society: *J.C.S.*, 1914, 105, 1131; *J.C.S.*, 1915, 107, 1685; *J.C.S.*, 1922, 121, 349; *J.C.S.*, 1923, 123, 2875. (*Signed by*) Alex. McKenzie, J. C. Irvine, John S. W. Boyle.

WARD, WILLIAM JOSEPH VICTOR, 41, Marlowe Rd., Cambridge. English. Research Student. 1st Class Natural Sciences Tripos, Part II, Chemistry 1924, Cambridge. (*Signed by*) W. J. Pope, W. G. Palmer, W. H. Mills.

WHIPP, JAMES EWART, 15, St. John's St., Longsight, Manchester. Pharmacist. Student of the Institute of Chemistry. Fellow of the Biochemical Society. Fellow of the Royal Microscopical Society. Member of the Society of Chemical Industry. (*Signed by*) Henry Garnett, Harry Brindle, Chas. Turner.

WHITEHEAD, ALAN DOUGLAS, "Trevorian," 90, West Hill, Putney, S.W. 15. British. Chemist. Student in Dept. of Chemistry, University College, London, Sessions 1921-22, 1922-23, 1923-24. B.Sc. (Lond.), Honours in Chemistry. (*Signed by*) F. G. Donnan, A. Groeves, W. E. Garner.

WILLIAMS, LESLIE THOMAS DOUGLAS, 23, Queen's Gate Gardens, S.W. 7. British. Student. Associateship of the Royal College of Science. I am now performing research at the above college and am desirous of keeping abreast with modern progress in science. (*Signed by*) G. A. R. Kon, M. A. Whiteley, H. L. Riley.

WYLDE, JOHN HENRY, 203, Boleyn Rd., Forest Gate, E. 7. English. Asst. Chemist, Laboratory of the Gas Light and Coke Coy, Stratford Station. Student at the East Ham Tech. College. National Cert. in Chemistry, Part-time Course, Higher or Advanced (distinction Inorganic Chemistry). City and Guilds of London, Gas Engineering, Ordinary and Honours. (*Signed by*) E. W. Griffiths, W. H. Barker, W. T. Clough.

YARSLEY, VICTOR EMMANUEL, The View, Highfield, Chasetown, nr. Walsall. British. Salter Research Fellow, 1924. B.Sc., 1st Hons., School of Chemistry, B'ham. Associate of the Institute of Chemistry. (*Signed by*) G. T. Morgan, H. D. K. Drew, C. E. Wood.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2).

NAIR, SADASHIV PARASHURAM, Nair Building, Lamington Road, Bombay. Indian (British subject). Pharmaceutical Chemist, i/o Powell's Pharma-

ceutical and Chemical Laboratory. Ph.G. (Boston). Graduate of the Massachusetts College of Pharmacy, Boston, Mass. Member of the American Pharmaceutical Association. At present working on finding out the commercial utility of some of the indigenous plants. My aim in joining the Society is to come in contact with the members of the Society and enjoy the privileges given by the same. (*Signed by*) H. B. Tilden.

SAN, MOUNG BA, B.A., 3, Stewart Road, Rangoon, Burma. Burmese. Assistant to the Chemical Examiner to the Government of Burma and Demonstrator in Physics and Chemistry at the Burma Government Medical School, Rangoon. Graduate of Calcutta University (1911-12). Winner of Chemistry Prize (term 1911-12) in the then Govt. College, Rangoon, now the Rangoon University College. No publications yet. 11 years' analytical experience in the Chemical Examiner's Laboratory, comprising examination of Mineral Oils, Drugs, Foodstuffs, Public Water supplies, and also Toxicological and Medico-legal analysis as well as Analysis of Ores, Minerals, and other commodities. (*Signed by*) Thein Kin, William Dallas.

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From the Publishers : Herren Urban & Schwarzenberg.

AMERICAN CERAMIC SOCIETY. Bibliography of magnesite refractories. Columbus 1924. pp. 8 + 41. (*Reference.*)

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From the Publishers : Messrs. Edward Arnold & Co.

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PHYSICS IN INDUSTRY. Lectures delivered before the Institute of Physics. Vol. II. By JOSEPH WILLIAM MELLOR, A. E. OXLEY, and CECIL HENRY DESCH. London 1924. pp. 48. ill. 3s. net. (*Recd.* 4/12/24.)

From the Publishers : The Oxford University Press.

REVUE GÉNÉRALE DES COLLOÏDES et de leurs applications industrielles. Year I, etc. Paris 1923 +. (*Reference.*)

From the Faraday Society.

SCHOTZ, SCHACHNA PEISACH. Synthetic organic compounds. London 1925. pp. 412. ill. 45s. net. (*Recd.* 19/12/24.)

From the Publishers : Messrs. Ernest Benn.

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ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. *Journal*. Vol. VII., etc. Washington 1923 +. (*Reference*.)

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certain metals including cerium, thorium, molybdenum, tungsten, radium, uranium, vanadium, titanium, and zirconium. (Bureau of Mines Bulletin, No. 212.) Washington 1923. pp. xviii + 326. ill. 3s. 6d. net. (*Recd.* 29/12/24.)

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RUSKA, JULIUS. *Arabische Alchemisten. II. Ġa'far alŠādiq, der sechste Imām. Mit einer Nachbildung der Handschrift Gotha A. 1292 (Haleb 338) in Manuldruck.* Heidelberg 1924. pp. 128 + 62. Gm. 7.20. (*Recd.* 1/12/24.)

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WEINLAND, RUDOLF. *Einführung in die Chemie der Komplex-Verbindungen (Wernersche Koordinationslehre) in elementarer Darstellung.* 2nd edition. Stuttgart 1924. pp. xx + 538. ill. Gm. 24. (*Recd.* 24/11/24.)

ZIPPERER, PAUL. *Die Schokoladen-Fabrikation: eine Monographie der Kakaofrucht und ihrer Verwertung.* 4th edition by HERMANN SCHAEFFER and — SCHRÖDER. Berlin 1924. pp. viii + 338. ill. \$5 net. (*Recd.* 13/12/24.)

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EVANS, EDWARD VICTOR. *Cantor Lectures on a study of the destructive distillation of coal.* London 1924. pp. 49. ill.

HUNTER, HAROLD. *The chemical significance of optical dispersion.* [London.] 1924. pp. 117. ill.

ROBINOVITCH, LOUISE G., and STILES, GEORGE W. *A chemical basis for the treatment of tuberculosis: experiments on the action*

of steapsin and insulin on tubercle bacilli. (From the *Amer. Rev. Tuberculosis*, 1924, 9.)

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. *Food Investigation Board*. Special Report No. 20. The problems of apple transport overseas: a general survey and summary of the results obtained by a scientific expedition to Australia in 1923. By FRANKLIN KIDD and CYRIL WEST. London 1924. pp. vi + 16. ill.

— *Fuel Research Board*. Technical Paper No. 10. Carbonisation of coal in continuous vertical retorts. A South Wales gas coal. (Mixture of Pentre and No. 3 Rhondda Seams from the Meiros Collieries, Llanharan.) London 1924. pp. iv + 26. ill.

SINNATT, FRANK STURDY, SIMPKIN, NEVILLE, and OWLES, ARCHIBALD BEWICK. The inorganic constituents of coal. Part IV. The melting point of coal ash. (*Lancs. & Cheshire Coal Research Assoc.* Bulletin No. 14.) London 1924. pp. 24. ill.

STERN, ARTHUR LANDAUER. Contributions to the chemistry of cellulose. I. Cellulose sulphuric acids. London 1894. pp. 28. (Two copies.)

TURNER, J. A. Mercurial poisoning: a report on poisoning from small quantities of mercurial vapor. (From the *U.S. Public Health Reports*, 1924, 39.)

UNITED STATES. *Department of Agriculture*. Department Bulletin No. 1149. Absorption and retention of hydrocyanic acid by fumigated food products. By EDWARD L. GRIFFIN [and others.] Washington 1923. pp. 16. ill.

— — Department Bulletin No. 1152. Soy and related fermentations. By MARGARET B. CHURCH. Washington 1923. pp. 26. ill.

— — Department Bulletin No. 1166. Apple by-products as stock foods. By G. P. WALTON and GEORGE L. BIDWELL. Washington 1923. pp. 40. ill.

— — Department Bulletin No. 1250. Relation between the composition of California cantaloupes and their commercial maturity. By EDWARD MACKAY CHANCE, C. G. CHURCH, and F. E. DENNY. Washington 1924. pp. 26. ill.

VOEGTLIN, CARL, JOHNSON, JAMES MCINTOSH, and DYER, HELEN. Viscosity and toxicity of arsphenamine solutions. (From the *U.S. Public Health Reports*, 1924, 39.)

WELCH, MARCUS BALDWIN. Notes on strength of timbers: with list of transverse tests on specimens in the Technological Museum. (*Sydney Technological Museum Bulletin*, No. 6.) Sydney 1923. pp. 12.

# PROCEEDINGS

OF THE

## CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, February 5th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The following were formally admitted Fellows of the Chemical Society: E. Lakeman, W. Kilroy, D. McKie, R. F. Barnes, and S. Krishnamurti.

Certificates were read for the first time in favour of:

- Niels Janniksen Bjerrum, Vendersgade 28, Copenhagen.  
James Herbert Clegg, West Cliffe, Queens Park Road, Burnley.  
Horace Cecil Cockroft, B.Sc., A.I.C., 6, Highfield Terrace, Halifax.  
Francis Xavier Coyne, 160, Addison Street, Blackburn.  
Robin George Westbury Farnell, A.R.C.S., A.I.C., Exeter College, Oxford.  
Richard Randolph Garran, B.Sc., Orphir, St. George's Road, Toorak, Melbourne.  
James Francis Halpin, F.I.C., 39, Benson Road, Forest Hill, S.E. 23.  
John Stanley Heaton, Ph.D., B.Sc., 43, Birch Road, Crumpsall, Manchester.  
John Cyril Hensman, M.A., A.I.C., Aldenham School, Elstree.  
Horace William Hughes, B.Sc., 27, Ombersley Road, Balsall Heath, Birmingham.  
David Bret Jehu, M.Sc., 34, High Street, Welshpool, Montgomeryshire.  
Clifford Merton Jones, B.Sc., Buxton Crescent, Newton Hill, Wakefield.  
David McDowall, 2, Kennishead Road, Thornliebank, Glasgow.  
Richard Alan Morton, B.Sc., Ph.D., A.I.C., 2, Lumley Street, Garston, Liverpool.  
Frederick Wilson Moulds, Hill Crest, Villa Road, Nottingham.  
David Pomerantz, 15, Nottingham Place, Commercial Road, E. 1.  
Robert Joseph Salmon, M.Sc., Holly Bank, Rowton, Chester.  
Tairain Singh Prem Chandra Sharma, M.Sc., Engineering College Hostel, Hindu University, Benares, India.  
John Robert Shepherd, M.Sc., A.I.C., Lady Hall Farm, Broughton-in-Furness.  
Leslie John Walker, 45, Devereux Road, Wandsworth Common, S.W. 18.  
William Alexander Waters, B.A., 35, Shirley Road, Cardiff.  
James Bernard Watson, 30, Mulgrave Road, West Hartlepool.

The following papers were read :

- "The chemistry of petroleum. Part I. The occurrence of compounds of sulphur in the light distillate from the crude oil of Maidan-i-Naftun." By S. F. BIRCH and W. S. G. P. NORRIS.
- "The chemistry of the three-carbon system. Part IV. A case of retarded mobility." By G. A. R. KON and R. P. LINSTAD.
- "Alternation in the molecular volumes of the normal monobasic fatty acids." By W. E. GARNER and E. A. RYDER.

Ordinary Scientific Meeting, Thursday, February 19th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society through the death of Dr. Horace T. Brown on February 6th, and announced that the Council had passed the following resolution :

"On behalf of the Chemical Society the Council desires to express its sense of the great loss the Society has sustained in the death of Dr. Horace T. Brown, who served on the Council as Vice-President, Ordinary Member of Council, Treasurer, and Foreign Secretary during a period of twenty years, and offers to his son and daughters deep sympathy in their bereavement."

Certificates were read for the first time in favour of :

- Janardhana Ram Bhatt, B.A., Sre Sumangala College, Panadura, Ceylon.
- Archibald Beresford Blunsden, The Bungalow, Westbury-on-Trym, Bristol.
- Thomas Henry Bowles, Allandale, Meadows Road, Cheam.
- William Harrison Brindley, M.C., M.A., M.Sc.Tech., A.I.C., 11, Millmoor Terrace, Glossop.
- Thomas James Elijah Gardner, 12, Bushwood Road, Kew.
- Helen Simpson Gilchrist, 82, North Street, St. Andrews.
- Frederick Denison Maurice Hocking, M.Sc., A.I.C., 18, Woodside Park Road, N. Finchley, N. 12.
- Joseph Taylor Jackson, B.Sc., 192, Algernon Road, Lewisham, S.E. 13.
- Ernest Edward Mabbott, B.Sc., 358, Fore Street, Edmonton, N. 9.
- Edgar Kent Palmer, B.Sc.Tech., Rose Bank, Victoria Road, Hale, Cheshire.
- John Brent Reed, B.Sc., A.I.C., 49, St. Mildred's Road, S.E. 12.
- George James Robertson, M.A., B.Sc., Ph.D., The Manse, Stratkinness St. Andrews.
- Leonard William Ernest Townsend, 35, Harewood Road, Collier's Wood, Merton, S.W. 19.
- Edwin John Woodcock, Stonecot, Claremont Hill, Jersey.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) :

- James Munsie Bell, Department of Chemistry, University of North Carolina, Chapel Hill, N.C., U.S.A.
- John Cameron, Peking Union Medical College, Peking, Chihli, N. China.
- Gordon McIntyre, B.Sc., Sarnia, Ontario, Canada.



Dr. B. Flürschheim and Dr. S. Sugden were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows :

- |   |  |
|---|--|
| Julius Nicholson Ashley, B.Sc., A.I.C.            | Jacob Kracovski, B.Sc.                             |
| George Alfred Bartram, B.Sc., A.I.C.              | Herbert Lambourne, M.A., M.Sc., F.I.C.             |
| George Harry Beeby, B.Sc., A.I.C.                 | John Joseph Laws.                                  |
| Arthur Henry Burdick Bishop.                      | Raymond James Wood Le Fevre.                       |
| Vincent Bloomer, B.Sc.                            | Alexander John Simpson Leiper, A.R.C.S.            |
| Claude McClellan Bottomley, B.Sc.                 | Alfred James Andrew Lennane, M.R.C.S., L.R.C.P.    |
| Frederick Stanley Brown, B.Sc., A.I.C.            | Frederick William Liley.                           |
| Percy Chorley, M.Sc.                              | James Gilbert Lunt, B.Sc.                          |
| Herbert Isaac Coombs, B.A., B.Sc.                 | William Hamilton McVicker, M.Sc.                   |
| Alexander Steven Corbet, Ph.D., B.Sc., A.I.C.     | Thomas Mann.                                       |
| William Houghton Crowe.                           | Vincent Mark Mascarenhas, B.A.                     |
| Alfred Davidson, B.Sc.                            | Frank Douglas Miles.                               |
| Ernest James Davis.                               | Sadashiv Parashuram Nair, Ph.G.                    |
| Walter Mark Duffin, B.Sc., A.R.C.S.               | Edward Arthur Nightingale.                         |
| Arthur Hynard Durrant.                            | Frederick William Offord.                          |
| Frederick John Eaton, Ph.D., B.Sc., A.I.C.        | Lionel Edward Outridge, B.Sc.                      |
| George Alfred Edwards, B.A., B.Sc.                | Thomas Webster Parker, A.R.C.S.                    |
| Harry Julius Emeléus, B.Sc., A.R.C.S.             | William Bayley Parker, F.I.C.                      |
| Ralph Margrave Esdaile.                           | Stuart Russell Parsons, B.Sc., A.I.C.              |
| Edward Hugh St. Clair Flack, M.Sc.                | William Samuel Payne.                              |
| Henry Bell Footner, B.Sc.                         | Kenneth John Pierson.                              |
| Desmond Geoghegan.                                | Richard Edwin Pike, B.Sc.                          |
| Clifton William Gibby, B.Sc., A.I.C.              | Douglas Victor Plumbridge, Ph.D., A.R.C.S., A.I.C. |
| Reginald Oswald Gibson, B.Sc., A.I.C.             | John Massey Preston, B.Sc., A.I.C.                 |
| Conrad Theodore Gimingham, F.I.C.                 | Richard Raper, B.A.                                |
| Jonathan Goodspeed.                               | John Frederick James Rule, B.Sc.                   |
| Richard Greenhalgh, B.Sc.                         | Moung Ba San, B.A.                                 |
| Robert Owen Griffith, M.Sc., A.I.C.               | Leslie Vivian Donald Scolah, B.Sc., A.I.C.         |
| Anthony James Hailwood, B.Sc.                     | George Frederick Sheppard.                         |
| Edward Stanley Hiscocks, B.Sc.                    | Joseph Thomas Shevlin.                             |
| Herbert Henry Hodgson, M.A., Ph.D., B.Sc., F.I.C. | Arthur Frederick Smethurst.                        |
| David Hughes.                                     | Ethel Minnie Snewing, B.Sc.                        |
| Kathleen Harriet Hughes.                          | Alton Ewart Clarence Smith.                        |
| Arthur Frederick Hunt, B.Sc.                      | Susanne Mabel Lavinia Snelus, A.I.C.               |
| Bertram Hobart Ingham, B.Sc.                      | Claude Hyman Spiers, M.A., Ph.D., B.Sc.            |
| John Dobney Johnson, B.Sc.                        | Harold Jacob Stern, Ph.D., B.Sc.                   |
| Wilford Jordayne Johnson.                         | Charles James Still, Ph.D., M.Sc.                  |
| Cecil Brellisford Oakes Jones.                    | Mohammad Hassan Syed, B.Sc.                        |
| William Wenallt Jones, M.Sc.                      | Mary Beatrice Thomas.                              |
| Alan Richmond Kennedy.                            | Eric Spencer Timms, B.Sc.                          |
| Frank Kenyon, A.I.C.                              | Eric Titterington.                                 |
| Frederick Ernest King.                            | Thomas Martin Aitken Tudhope, Ph.D., B.Sc.         |
| Eric Knott.                                       |  |

Charles Cyril Norrey Vass, B.Sc.  
 John Harry Village, B.Sc.  
 Israel Vogel, B.Sc.  
 John Wilson, M.Sc.  
 Nellie Walker, M.A., Ph.D., B.Sc.  
 William Joseph Victor Ward, B.A.  
 James Ewart Whipp.

Alan Douglas Whitehead, B.Sc.  
 Leslie Thomas Douglas Williams,  
 A.R.C.S.  
 John Henry Wyld.  
 Victor Emmanuel Yarsley, B.Sc.,  
 A.I.C.

The following paper was read :

- "The nature of the alternating effect in carbon chains. Part II. The directing influence of the  $\alpha$ -methoxyvinyl group in aromatic substitution." By C. K. INGOLD and E. H. INGOLD.  
 Dr. T. SLATER PRICE discussed "The action of light on the photographic plate."

### ANNUAL GENERAL MEETING.

The Annual General Meeting will take place on Thursday, March 26th, 1925, at 4 p.m., when the PRESIDENT, Professor W. P. WYNNE, D.Sc., F.R.S., will deliver his Address.

### ANNIVERSARY DINNER.

The Anniversary Dinner will be held in the Grand Hall of the Hotel Victoria, Northumberland Avenue, W.C.2., on Thursday, March 26th, 1925 (the day of the Annual General Meeting), at 7 for 7.30 p.m. The presence of ladies will be welcomed.

Tickets, price 12s. 6d. each (including gratuities to waiters) can be obtained from the Assistant Secretary. It will facilitate arrangements if Fellows will apply for tickets at an early date, in any event before March 19th.

List of Papers, or Abstracts thereof, received between January 16th and February 19th, 1925. (This list does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"Colour and molecular geometry. Part III. A graphical presentation of the theory." By J. MOIR.

"Tesla-luminescence spectra. Part V. Some polynuclear hydrocarbons." By W. H. McVICKER, J. K. MARSH, and A. W. STEWART.

"The surface tensions of aqueous solutions of various organic compounds." By P. R. EDWARDS.

- "The cryoscopic method for adsorption." By H. L. RICHARDSON and P. W. ROBERTSON.
- "Ring-chain tautomerism. Part XII. Derivatives of  $\alpha$ -ethyl- $\beta\beta$ -dimethylglutaric acid." By G. A. R. KON, L. F. SMITH, and J. F. THORPE.
- "A determination of the melting and transition points of potassium dichromate." By P. L. ROBINSON, G. E. STEPHENSON, and H. V. A. BRISCOE.
- "Interaction of hydrogen and carbon dioxide on the surface of platinum." By C. R. PRITCHARD and C. N. HINSHELWOOD.
- "The identity of uncineol with eudesmol." By A. R. PENFOLD.
- "Further X-ray measurements on long-chain compounds ( $n$ -hydrocarbons)." By A. MÜLLER and W. B. SAVILLE.
- "An X-ray investigation of the ketone series." By W. B. SAVILLE and G. SHEARER.
- "The relationship of thyroxin to tryptophane." By C. S. HICKS.
- "A new method of flame analysis." By O. C. DE C. ELLIS and H. ROBINSON.
- "The movement of flame in closed vessels." By O. C. DE C. ELLIS and R. V. WHEELER.
- "*cyclo*Telluropentanediones containing aliphatic and aromatic substituents." By G. T. MORGAN and C. J. A. TAYLOR.
- "3-Chlorobenzopyrylium derivatives." By L. R. RIDGWAY and R. ROBINSON.
- "A qualitative test for weak bases." By R. ROBINSON.
- "The labile nature of the halogen atom in organic compounds. Part X. The action of hydrazine hydrate on the halogen derivatives of  $\alpha$ -nitro-fatty acids." By A. K. MACBETH and D. TRAILL.
- "The effect of colloids on the replacement of lead and copper from their salts by zinc." By L. T. M. GRAY.
- "A new portable apparatus for the analysis of illuminating and other gases." By H. D. MURRAY.
- "The action of halogen on phenylhydrazones. Part II. The action of chlorine." By J. E. HUMPHRIES, H. HUMBLE, and R. EVANS.
- "Anomalous adsorption." By J. B. SPEAKMAN and A. E. BATTYE.
- "The photo-decomposition of chlorine water and of aqueous hypochlorous acid solutions. Part I." By A. J. ALLMAND, P. W. CUNLIFFE, and R. E. W. MADDISON.
- "Studies of dynamic isomerism. Part XVII. The mutarotation of aluminium benzoyl-camphor." By I. J. FAULKNER and T. M. LOWRY.

- "Studies of dynamic isomerism. Part XVIII. The mechanism of mutarotation and of hydrolytic and prototropic change; with a criticism of Baker, Ingold, and Thorpe's doctrine of non-intervention." By T. M. LOWRY.
- "Studies of dynamic isomerism. Part XIX. Experiments on the arrest of mutarotation in tetramethylglucose." By T. M. LOWRY and E. M. RICHARDS.
- "The freezing points of hydrofluoric acid." By J. D. C. ANTHONY and L. J. HUDLESTON.
- "The hydrolysis of iodine as measured by the iodine electrode." By H. D. MURRAY.
- "Some aromatic chlorovinylarsines." By A. F. HUNT and E. E. TURNER.
- "The mechanism of the reaction between arylhydrazine sulphonic acids and acetoacetic ester." By G. REEVES.
- "The compounds formed by the action of bromine upon benzaldehyde-phenylhydrazine." By F. D. CHATTAWAY and A. J. WALKER.
- "Periodic electrochemical phenomena." By E. S. HEDGES and J. E. MYERS.
- "The nitration of meta-hydroxybenzaldehyde carbonate and ethyl carbonate." By F. A. MASON.
- "A synthesis of 1 : 2-dihydroquinaldine." By F. A. MASON.
- "The synthesis of 5 : 5'-dibromo-6 : 6'-dimethoxy thioindigo." By R. H. GRIFFITH and E. HOPE.
- "The interaction of sodium chloride and alumina." By F. H. CLEWS.
- "A resolution of benzoin." By F. J. WILSON and I. V. HOPPER.
- "Semicarbazones of benzoin. Part I." By I. V. HOPPER.
- "The 'activation' of graphite as a sorbent of oxygen." By D. H. BANGHAM and J. STAFFORD.
- "The mechanism of the formation of malachite from basic cupric carbonate." By J. R. I. HEPBURN.
- "A synthesis of oxyberberine. Part I." By W. H. PERKIN, J. N. RÂY, and R. ROBINSON.
- "Variation of colour in the fluoresceine family." By J. MOIR.
- "The equilibria underlying the soap boiling processes. Pure sodium palmitate." By J. W. MCBAIN and G. M. LANGDON.
- "Some reactions of triethylphosphine." By J. N. COLLIE.
- "Nitro- and amino-ethoxy-lutidine." By J. N. COLLIE and G. BISHOP.

## ADDITIONS TO THE LIBRARY.

I. *Donations.*

ADAMKIEWICZ, ALBERT. Die Natur und der Nährwerth des Peptons: eine experimentelle Untersuchung zur Physiologie des Albumins. Berlin 1877. pp. viii + 128. From Dr. H. E. Cox.

ALLEN, ROBERT. Bismuth ores. (Imperial Institute Monograph on Mineral Resources.) London 1925. pp. x + 62. ill. 3s. 6d. net. (*Recd.* 5/3/25.) From the Director.

ATAACK, FREDERICK WILLIAM, assisted by LEONARD WHINYATES. The Chemists' Year Book 1924. American data in collaboration with FRANCIS M. TURNER, JR. Manchester [1924]. pp. xii + 1164. ill. (*Reference.*) From Mr. L. Eynon.

BÖTTGER, WILHELM. Qualitative Analyse und ihre wissenschaftliche Begründung. 4th—7th edition. Leipzig 1925. pp. xvi + 644 + 34. M. 22. (*Recd.* 3/2/25.)

From the Publisher: Herr Wilhelm Engelmann.

CARPENTER, LEONARD. Mechanical mixing machinery. London 1925. pp. 138. ill. 6s. net. (*Recd.* 11/2/25.)

From the Publishers: Messrs. Ernest Benn.

CONGRÈS INTERNATIONAL POUR LA RÉPRESSION DES FRAUDES. Compte rendu des travaux du deuxième Congrès, 1909. Paris 1910. pp. viii + 1496. From Dr. H. E. Cox.

DEADLY ADULTERATION and slow poisoning unmasked; or, disease and death in the pot and the bottle. By an enemy to fraud and villany. New edition. London [n. d.]. pp. viii + 190. From Dr. H. E. Cox.

ELLIOTT, CYRIL. Distillation principles. London 1925. pp. 166. ill. 6s. net. (*Recd.* 11/2/25.)

From the Publishers: Messrs. Ernest Benn.

GIBBS, WILLIAM E. The dust hazard in industry. London 1925. pp. 168. ill. 6s. net. (*Recd.* 11/2/25.)

From the Publishers: Messrs. Ernest Benn.

GORE, GEORGE, SPARLING, MARCUS, and SCOFFERN, JOHN. Practical chemistry: including the theory and practice of electro-deposition; photographic art; the chemistry of food, with a chapter on its adulterations; and the chemistry of artificial illumination. London 1856. pp. xvi + 574. ill. From Dr. H. E. Cox.

GUYE, CHARLES EUGÈNE. Physico-chemical evolution. Translated by J. R. CLARKE. London 1925. pp. xii + 172. 6s. net. (*Recd.* 12/2/25.) From the Publishers: Messrs. Methuen & Co.

HALSE, EDWARD. Antimony ores. (Imperial Institute Monograph on Mineral Resources.) London 1925. pp. x + 102. ill. 5s. net. (*Recd.* 5/3/25.) From the Director.

HENNINGER, ARTHUR [RODOLPHE MARIE]. De la nature et du rôle physiologique des peptones. Paris 1878. pp. 68.

From Dr. H. E. Cox.

HOFMANN, FRANZ. Die Bedeutung von Fleischnahrung und Fleischconserven mit Bezug auf Preisverhältnisse. Leipzig 1880. pp. iv + 120.

From Dr. H. E. Cox.

JANKE, ALEXANDER. Allgemeine technische Mikrobiologie. I Teil: Die Mikroorganismen. Dresden 1924. pp. xii + 342. ill. M. 12. (Recd. 3/2/25.) From the Publisher: Herr Theodor Steinkopff.

LOWY, ALEXANDER, and HARROW, BENJAMIN. An introduction to organic chemistry. New York 1924. pp. x + 390. ill. 15s. net. (Recd. 12/2/25.)

From the London Publishers: Messrs. Chapman & Hall.

PATTERSON, AUSTIN M. A German-English dictionary for chemists. 5th printing, with addenda. New York 1924. pp. xvi + 344. (Reference.) 12s. 6d. net.

From the London Publishers: Messrs. Chapman & Hall.

REVUE GÉNÉRALE DES COLLOÏDES et de leurs applications industrielles. Year I, etc. Paris 1923 +. (For circulation.)

From the Biochemical Society.

SEYMOUR, HARTLAND. Agitating, stirring and kneading machinery. London 1925. pp. 140. ill. 6s. net. (Recd. 11/2/25.)

From the Publishers: Messrs. Ernest Benn.

SPIELMANN, PERCY EDWIN. Bituminous substances: scientific progress of practical importance during the last fifteen years. London 1925. pp. xvi + 206. ill. 15s. net. (Recd. 21/1/25.)

From the Publishers: Messrs. Ernest Benn.

TUNGAY, SYDNEY J. Acid-resisting metals. London 1925. pp. 136. ill. 6s. net. (Recd. 11/2/25.)

From the Publishers: Messrs. Ernest Benn.

URBAIN, GEORGES. Les notions fondamentales d'élément chimique et d'atome. Paris 1925. pp. iv + 172. 10 fr. (Recd. 10/2/24.)

From the Publishers: MM. Gauthier-Villars et Cie.

WELLINGS, A. W. Chemical symbols, formulæ and calculations. London 1925. pp. viii + 96. 3s. net. (Recd. 16/1/25.)

From the Publishers: Messrs. Methuen & Co.

## II. By Purchase.

ARENDT, RUDOLF. Technik der Experimentalchemie: Anleitung zur Ausführung chemischer Experimente. 5th edition. Edited by LUDWIG DOERMER and WALTER FRANCK. Leipzig 1925. pp. xxviii + 732. ill. M. 26.50. (Recd. 2/2/25.)

FREUNDLICH, HERBERT. The elements of colloidal chemistry. Translated by GEORGE BARGER. London 1925. pp. viii + 210. ill. 7s. 6d. net. (Recd. 19/1/25.)

# PROCEEDINGS

## OF THE

### CHEMICAL SOCIETY.

Lecture, held in the Lecture Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W. 1, on Thursday, February 26th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

Sir WILLIAM HARDY, M.A., Sec.R.S., delivered his Lecture entitled: "Problems presented by Films on Solid Surfaces." A vote of thanks to the Lecturer, proposed by Professor H. E. Armstrong, F.R.S., seconded by Professor A. V. Hill, F.R.S., and supported by the Chairman, was carried with acclamation, and acknowledged by Sir William Hardy.

Ordinary Scientific Meeting, Thursday, March 5th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
Sir Edward Thorpe .....	Feb. 16th, 1871.	Feb. 23rd.
Alexander Mitchell Williams .....	Dec. 7th, 1922.	Feb. 21st.

The PRESIDENT also announced that at a Special Meeting of the Council, held on February 26th, 1925, the following resolution was passed:

"On behalf of the Chemical Society, the Council desires to express its profound regret at the death of Sir Edward Thorpe, who for 54 years was a Fellow, and during 39 years served the Society as Member of Council, Vice-President, Treasurer and President, and while Treasurer initiated and supervised the production of the first three volumes of the Collective Indexes of the Society's Journal.

"The Council recognises that by Sir Edward Thorpe's death the

Society loses a wise counsellor and British Chemistry a distinguished investigator, and offers to Lady Thorpe its sincere sympathy in her bereavement."

The Fellows present expressed their concurrence in this resolution by rising from their places.

It was also announced that

(1) With a view to increasing the usefulness of the Library, the Council has made arrangements for the photographic copying by means of the Photostat, of material contained in the Library. Particulars as to cost, etc., can be obtained from the Librarian.

(2) The first lecture in connection with the Fison Memorial Fund, which was established to endow a Lectureship in memory of the late Dr. A. H. Fison, will be delivered by Professor J. J. Thomson, O.M., F.R.S., on Thursday, May 7th, 1925, at 5 p.m., the Right Hon. the Earl of Balfour presiding. The place of meeting will be announced later. Tickets of admission will be obtainable from Mr. S. E. Carr.

The following List of Nominations for vacant places on the Council was read from the Chair :

President : Arthur W. Crossley.

Vice-Presidents who have filled the office of President (3 vacancies) : H. E. Armstrong, A. Scott, W. P. Wynne.

Vice-Presidents who have not filled the office of President (2 vacancies) : J. B. Cohen, N. V. Sidgwick.

Secretary : T. Slater Price.

Foreign Secretary : F. G. Donnan.

Ordinary Members of Council :

(a) Town Members, *i.e.*, those resident within 50 miles of Charing Cross (5 vacancies) : H. Bassett, F. W. Gamble, J. Kenyon, B. D. Porritt, G. Stubbs.

(b) Country Members, *i.e.*, those resident beyond 50 miles from Charing Cross (2 vacancies) : F. A. Freeth, W. Rintoul, F. J. Wilson.

Dr. P. W. Austin and Dr. E. E. Turner were appointed Scrutators to assist in the counting of votes recorded in the election of the Country Members of Council.

The following were formally admitted Fellows of the Chemical Society : F. H. Banfield, F. Kenyon, A. H. Durrant, A. F. Smethurst, J. D. Johnson, R. E. Pike, C. H. Spiers, S. Dutt, J. Kracovski, H. J. Emeléus, I. Vogel, K. V. Thimann, S. S. G. Sircar, B. T. Narayanan.



The Treasurer drew attention to the fact that on Thursday, March 5th, 1885, exactly 40 years ago, a certificate of a candidate for election as a Fellow was read for the first time in favour of William Palmer Wynne. Commenting on the uniqueness of the occasion, the Treasurer expressed the hope that the President would long be spared to give the Society the benefit of his wise counsel. The meeting showed its hearty approval of the Treasurer's remarks, and the President expressed his sincere thanks for the kind reference.

Certificates were read for the first time in favour of :

Geoffrey Alger Blyde, East Cliffe, East Bank Road, Sheffield.

Frank Henry Charles Bull, B.Sc., A.I.C., 50, Cornwall Road, Bishopston, Bristol.

Harry Dean, 134, New Lane, Oswaldtwistle.

Irvine John Faulkner, Emmanuel College, Cambridge.

Thomas Flett, B.Sc., A.I.C., Anchor Cottage, Kirkwall, Orkney.

John Charles Giblin, B.Sc., A.I.C., 3, Kensington Terrace, Brecon.

Isabel Hodgson Hadfield, M.Sc., 65, Langham Road, Teddington.

Thomas Haworth, 8, Park Terrace, Fielding Lane, Oswaldtwistle.

William Jobson, 52, The Mall, Swindon.

Thomas William Jones, B.Sc., 36, St. Vincent Road, Westcliff-on-Sea.

John Keane, M.Sc., Ph.D., 6 Shamrock Villas, Drumcondra, Dublin.

Andrew Joseph Myles, 12, Gardner Road, Tue Brook, Liverpool.

Alfred William Nash, B.Sc., 18, Prospect Road, Moseley, Birmingham.

Henry Bowen Oakley, M.Sc., A.R.C.S., Wellcome Tropical Research Laboratories, Khartoum.

Harry Rawlings, B.Sc., 15, Station Road, Ramsey, Huntingdon.

Alan Lawrence Smith, M.Sc., 22, Dean Street, Blackpool.

George Thorn, B.Sc., Grove House, Beechen Grove, Watford.

Ernest Swann Watts, Eaglesfield, Limefield Road, Kersal, Manchester.

Archibald Steele Whamond, 22, Church Street, Alloa.

John Stanley Worthington, 27, Rowena Street, Great Lever, Bolton.

The following papers were read :

"Studies of dynamic isomerism. Part XVII. The mutarotation of aluminium benzoylcamphor." By I. J. FAULKNER and T. M. LOWRY.

"Studies of dynamic isomerism. Part XVIII. The mechanism of mutarotation, and of hydrolytic and prototropic change; with a criticism of Baker, Ingold, and Thorpe's doctrine of non-intervention." By T. M. LOWRY.

"Studies of dynamic isomerism. Part XIX. Experiments on the arrest of mutarotation in tetramethylglucose." By T. M. LOWRY and E. M. RICHARDS.

Ordinary Scientific Meeting, Thursday, March 19th, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through the death of Joseph Arderne Ormerod, who was elected a Fellow on May 16th, 1872, and died on March 5th.

R. H. Purcell was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of :

James Lindsay Buchan, B.Sc., Hampden Club, N.W. 1.  
 John Alfred Valentine Butler, M.Sc., The Potteries, Winchcombe, Glos.  
 Annie Lavinia Byford, B.Sc., 73, Elderton Road, Westcliff-on-Sea.  
 James Craik, M.A., B.Sc., Ph.D., The University, St. Andrews.  
 Herbert Greetham Dane, M.Sc., The Diocesan Training College, Winchester.  
 Margaret Stedman Leonora Dixon, Homebush, Worcester Road, Sutton.  
 Donald Hanson, 7, Willow Bank, Halifax.  
 Joseph Hill, 58, Spring Street, Accrington.  
 Jim Hoyle, 11, Crow Lane, Ramsbottom.  
 Richard H. F. Manske, M.Sc., The University, Manchester.  
 Hugh Clonston Moir, B.Sc., A.I.C., 7, Craigielea Street, Dennistoun, Glasgow.  
 William George Rhodes, 318, Granville Road, Park, Sheffield.  
 Thomas Kennedy Walker, M.Sc., Ph.D., F.I.C., 4, Swythamley Road, Cheadle Heath, Stockport.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) in favour of :

Karl Thomas, M.D., The University, Leipzig.  
 Frederic N. Williams, P.O. Box 1117, Shreveport, La., U.S.A.

The following papers were read :

- "The 'activation' of graphite as a sorbent of oxygen." By D. H. BANGHAM and J. STAFFORD.
- "Ring-chain tautomerism. Part XIV. The structure of Balbiano's acid." By E. ROTHSTEIN, A. STEVENSON, and J. F. THORPE.
- "The tendency towards intramolecular condensation in cyclic keto-esters. Part I. The formation and disruption of bicyclic dihydroresorcinols." By E. H. FARMER and J. ROSS.
- "The structure of the enolic forms of  $\beta$ -ketoesters and  $\beta$ -diketones." By N. V. SIDGWICK.

### PUBLICATIONS FUND.

In connection with the Appeal for the Publications Fund issued by the Treasurer, it has been decided that a list of donations and subscriptions received shall appear in the Proceedings for June. All donations and subscriptions received prior to the end of May will be included in the List.

## LIST OF FELLOWS, 1925.

It has been decided to print the List of Fellows for 1925 and to supply the List to those Fellows who make application to the Assistant Secretary by the 31st July, 1925.

List of Papers, or abstracts thereof, received between February 19th and March 19th, 1925. (This List does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

- "The isomerism of the oximes. Part XXI. Action of picryl chloride and of 2:4-dinitrochlorobenzene on aldoximes." By O. L. BRADY and L. KLEIN.
- "Derivatives of semioxamazide. Part III." By F. J. WILSON and E. C. PICKERING.
- "The stereochemistry of the hydronaphthalenes and related sesquiterpenes. Part I. Decahydro- $\beta$ -naphthoic acid." By F. W. KAY and N. STUART.
- "Irregularities in the condensation of certain nitriles with resorcinol." By E. CHAPMAN and H. STEPHEN.
- "Studies in the benzothiazole series. Part III. The pseudobases of the *l*-substituted benzothiazole quaternary salts." By L. M. CLARK.
- "Sulphur compounds removed from a Persian petroleum by means of sulphuric acid. Part I." By E. H. THIERRY.
- "Ring-chain tautomerism. Part XIII. Three carbon ring-chain tautomerism in a bridged ring system." By J. W. BAKER.
- "The measurement of the dielectric constants of liquids." By H. HARRIS.
- "Note on the physiological action of certain benzothiazoles and mercaptan derivatives." By R. F. HUNTER.
- "Note on the physiological action of certain arylamino-derivatives of monochloroacetic acid." By R. F. HUNTER.
- "The hydrolytic properties of certain amino-acids." By L. P. BOSMAN.
- "The reduction of anethole nitrosochloride." By J. B. SHOESMITH and R. H. SLATER.
- "Investigations on the dependence of rotatory power on chemical constitution. Part XXV. Three optically active alcohols containing a phenyl group and some esters derived therefrom." By L. F. HEWITT and J. KENYON.
- "The integral relations between the vibration frequencies of molecules." By E. C. C. BALY, R. A. MORTON, and E. ROGERS.

- "The photochemical decomposition of nitrosyl chloride." By E. J. BOWEN and J. F. SHARP.
- "Ray's supposed triethylene trisulphide." By G. M. BENNETT and W. A. BERRY.
- "Hepta- and nono-dilactones." By G. M. BENNETT.
- "A synthesis of pyrylium salts of anthocyanidin type. Part VI. Polyhydroxyflavylium salts related to chrysin, apigenin, loto-flavin, luteolin, galangin, fisetin, and morin." By D. D. PRATT and R. ROBINSON.
- "Reactions depending upon the vapour at the interface of two immiscible liquids. Part II." By G. HARKER and R. K. NEWMAN.
- "The hydrates of calcium carbonate." By J. HUME.
- "The labile nature of the halogen atom in organic compounds. Part XI. The halogenation of acetylsuccinic ester." By A. K. MACBETH and D. TRAILL.
- "A solid hydride of antimony." By E. J. WEEKS and J. G. F. DRUCE.
- "A study of the effect of the concentration of aqueous sodium hydroxide solutions upon the rate of saponification of olive oil." By G. I. FINCH and A. KARIM.
- "The formation of *d*-2:2:4-trimethylcyclohexan-3-one-1-carboxylic acid from *d*-camphorquinone." By C. S. GIBSON and J. L. SIMONSEN.
- "The reaction between aromatic aldehydes and phenanthraquinone in presence of ammonia." By A. C. SIRCAR and N. C. G. RAY.
- "Studies in heterocyclic compounds. Part I." By A. C. SIRCAR and P. K. DE.
- "The action of azides on toluquinone." By F. D. CHATTAWAY and G. D. PARKES.
- "The partial pressures of water vapour and of sulphuric acid vapour over concentrated solutions of sulphuric acid at high temperatures." By J. S. THOMAS and W. F. BARKER.
- "Investigations on the dependence of rotatory power on chemical constitution. Part XXVI. Four alcohols containing the vinyl group and some esters derived therefrom." By J. KENYON and D. R. SNELGROVE.
- "A synthesis of pyrylium salts of anthocyanidin type. Part VII. The preparation of the anthocyanidins with the aid of tri-acetylphloroglucinaldehyde." By D. D. PRATT and R. ROBINSON.
- "A synthesis of pyrylium salts of anthocyanidin type. Part VIII. A new synthesis of pelargonidin chloride and of galanginidin chloride." By T. MALKIN and R. ROBINSON.

- "The action of halogens upon *m*- and *p*-nitrobenzaldehyde phenylhydrazones." By F. D. CHATTAWAY and A. J. WALKER.
- "Plant cuticles. Part I. Modern plant cuticles. Studies in the composition of coal." By V. H. LEGG and R. V. WHEELER.
- "The explosion of ammonia with carbon monoxide and oxygen." By J. W. BEESON and J. R. PARTINGTON.
- "3 : 3-Diethylpentane (tetraethylmethane)." By G. T. MORGAN, S. R. CARTER, and A. E. DUCK.
- "Aromatic esters of acylecgonines." By W. H. GRAY.
- "The additive formation of four-membered rings. Part VII. The synthesis and division of some dimethylene-1 : 3-oxamines." By C. K. INGOLD.
- "The decomposition of hydrogen peroxide by cobaltic hydroxide." By F. G. TRYHORN and G. JESSOP.

## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

ACTUALITÉS DE CHIMIE CONTEMPORAINE. Publiées sous la direction de ALBIN HALLER. 3rd series. Paris 1925. pp. viii + 328. 12 fr. net. (*Recd.* 24/2/25.)

From the Publisher : M. Gaston Doin.

HANDBUCH DER SALVARSANTHERAPIE. Edited by W. KOLLE and K. ZIELER. Vol. II. Berlin 1925. pp. xiv + 878. ill. *M.* 34.40. (*Recd.* 16/3/25.) From the Publishers : Messrs. Urban & Schwarzenberg.

### II. *By Purchase.*

GMELINS HANDBUCH DER ANORGANISCHEN CHEMIE. 8th edition. By RICHARD JOSEF MEYER [and others]. Berlin 1924 +. (*Reference.*)

GNAMM, H. Die Gerbstoffe und Gerbmittel. (Chemie in Einzeldarstellungen, Vol. XII.) Stuttgart 1925. pp. xvi + 394. *M.* 24. (*Recd.* 14/3/25.)

HANSLIAN, RUDOLF, and BERGENDORFF, FR. Der chemische Krieg : Gasangriff, Gasabwehr und Raucherzeugung. Berlin 1925. pp. iv + 226. ill. *M.* 11. (*Recd.* 10/2/25.)

HOLDE, DAVID. Kohlenwasserstofföle und Fette sowie der ihnen chemisch und technisch nahestehenden Stoffe. 6th edition. Berlin 1924. pp. xxviii + 856. ill. *M.* 45. (*Recd.* 2/2/25.)

HOPPE-SEYLER, ERNST FELIX IMMANUEL. Handbuch der physiologisch- und pathologisch-chemischen Analyse. 9th edition. By HANS THIERFELDER. Berlin 1924. pp. xvi + 1004. ill. *M.* 69. (*Recd.* 2/2/25.)

KLÖCKER, ALB. Die Gärungsorganismen in der Theorie und Praxis der Alkoholgärungsgewerbe. 3rd edition. Berlin 1924. pp. xviii + 448. ill. *Rm.* 12. (*Recd.* 24/2/25.)

LEBERLE, HANS. Die Bierbrauerei. 2 vols. Stuttgart 1921-25. pp. xii + 307, xii + 589. ill. *M.* 31.80. (*Recd.* 9/3/25.)

LORD, NATHANIEL WRIGHT, and DEMOREST, DANA J. Metallurgical analysis. 5th edition. New York 1924. pp. xxii + 472. ill. 20s. net. (*Recd.* 19/1/25.)

MILLIKAN, ROBERT ANDREWS. The electron: its isolation and measurement and the determination of some of its properties. 2nd edition. Chicago 1924. pp. xiv + 293. ill. 8s. 9d. net. (*Recd.* 19/1/25.)

MÜLLER, ERICH. Elektrochemisches Praktikum. 4th edition. Dresden 1924. pp. xvi + 264. ill. *M.* 10. (*Recd.* 28/1/25.)

NERNST, WALTHER. Die theoretischen und experimentellen Grundlagen des neuen Wärmesatzes. 2nd edition. Halle (Saale) 1924. pp. viii + 232. ill. *M.* 12. (*Recd.* 10/2/25.)

RISTENPART, EUGEN. Chemische Technologie der organischen Farbstoffe. 2nd edition. Leipzig 1925. pp. xiv + 300 + 12 pattern plates. ill. *M.* 15. (*Recd.* 2/2/25.)

SOMMERFELD, ARNOLD. Atombau und Spektrallinien. 4th edition. Braunschweig 1924. pp. xii + 862. ill. *M.* 22. (*Recd.* 28/1/25.)

STRACHE, HUGO, and LANT, RICHARD. Kohlenchemie: Entstehung und chemisches Verhalten der Kohlen und ihrer Bestandteile, Untersuchungen der Kohlen. Leipzig 1924. pp. xvi + 600. ill. *M.* 24. (*Recd.* 2/2/25.)

SUTTON, FRANCIS. A systematic handbook of volumetric analysis. 11th edition. Revised throughout, with numerous additions, by WILLIAM LINCOLNE SUTTON and ALFRED EDWARD JOHNSON. London 1924. pp. x + 630. ill. 35s. net. (*Recd.* 19/1/25.)

TAYLOR, HUGH STOTT. [Editor.] A treatise on physical chemistry: a co-operative effort by a group of physical chemists. 2 vols. London 1924. pp. xii + 604 + 42, x + 701 to 1360 + 42. ill. 50s. net. (*Recd.* 21/1/25.)

### III. Pamphlets.

COHEN, BARNETT, GIBBS, HARRY DRAKE, and CLARK, WILLIAM MANSFIELD. Studies on oxidation-reduction. VI. A preliminary study of indophenols: (a) dibromo substitution products of phenol indophenol; (b) substituted indophenols of the ortho type; (c) miscellaneous. (From the *U.S. Public Health Reports*, 1924, 39.)

ELVOVE, ELIAS. A method for the estimation of total sulfur in neocarsphenamine and sulpharsphenamine. (From the *U.S. Public Health Reports*, 1924, 39.)

# PROCEEDINGS

## OF THE

# CHEMICAL SOCIETY.

### ANNIVERSARY DINNER.

THE Anniversary Dinner of the Society was held in the Grand Hall, Hotel Victoria, on Thursday, March 26th, 1925, at 7 for 7.30 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair. The following is a list of those present :

Aeschlimann, J. A.	Carr, Miss M.
Anderson, Rt. Hon. Sir John, G.C.B., <i>Permanent Under-Secretary of State for Home Affairs.</i>	Carr, S. E., <i>Assistant Secretary.</i>
Anderson, Miss O. R.	Chapman, A. Chaston, F.R.S.
Armstrong, H. E., F.R.S., <i>Past- President.</i>	Chapman, Mrs. Chaston.
Armstrong, Miss N.	Chapman, A. W.
Austin, P. C.	Chattaway, F. D., F.R.S.
Austin, Mrs. P. C.	<i>Chemical Age.</i>
Backer, H. J.	<i>Chemistry and Industry.</i>
Baker, H. B., C.B.E., F.R.S.	Clifford, E.
Baker, Mrs. H. B.	Clifford, F. W., <i>Librarian.</i>
Baly, E. C. C., C.B.E.	Coates, J. E., O.B.E.
Bassett, H.	Cod, L. M.
Bennett, Miss D. M.	Cohen, Ernst, <i>Nederlandsche Chemische Vereeniging.</i>
Bennett, J. C. S.	Cohen, Mrs. E.
Bennett, G. M.	Collins, S. W.
Bolton, E. R.	Cooper, A. J. Bullen.
Bolton, Mrs. E. R.	Cooper, H. Creemer.
Bolton, L. H.	Corfield, C. E.
Bolton, Mrs. L. H.	Corfield, Mrs. C. E.
Boyd, D. R.	Crossley, A. W., C.M.G., C.B.E., F.R.S., <i>President.</i>
Brady, O. L.	Crossley, Mrs. A. W.
Brewer, F. M.	Crossley, K. H.
Brown, R. B.	<i>Daily Telegraph.</i>
Brown, Mrs. R. B.	Dale, H. H., C.B.E., F.R.S.
Burch, W. J. N.	Desch, C. H., F.R.S.
Burgess, W. T.	Dickes, Miss W. E.
Burton, H.	Donald, M. B.
Carr, F. H., C.B.E.	Donnan, F. G., C.B.E., F.R.S., <i>Foreign Secretary.</i>
Carr, Mrs. F. H.	Donnan, Miss.

- Drew, R. B.  
 Druce, J. G. F.  
 Drummond, J. C.  
 Drummond, Mrs. M. H.  
 Dudley, H. W., O.B.E.  
 Dudley, Mrs.  
 Duncalfe, R.  
 Dunn, F. P.  
 Dyer, B.  
 Dyer, Mrs. B.  
 Eldridge, A. A.  
 Eldridge, Mrs. A. A.  
 Ellingham, H. J. T.  
 Fargher, R. G.  
 Fox, J. J., O.B.E.  
 Freeth, F. A., O.B.E.  
 Galletly, W. G.  
 Gardner, J. A.  
 Garner, W. E.  
 Gibbons, W. M., O.B.E., *Registrar, Sheffield University.*  
 Gibson, C. S., O.B.E., *Secretary.*  
 Gilling, C.  
 Gordon, J. G.  
 Gray, J. Hunter, K.C.  
 Gray, Mrs. J. Hunter.  
 Gray, W. H.  
 Greenaway, A. J.  
 Greeves, A.  
 Greeves, Mrs. A.  
 Gregory, Sir Richard.  
 Griffiths, O. S.  
 Haas, P.  
 Hamer, Miss F. M.  
 Hamer, J. C.  
 Hamer, Sir William.  
 Hamer, Lady.  
 Heath, Sir Frank, K.C.B., *Secretary, Department of Scientific and Industrial Research.*  
 Henderson, G. G., F.R.S., *President, The Institute of Chemistry.*  
 Henry, T. A.  
 Henry, Mrs. T. A.  
 Hewitt, J. T., F.R.S.  
 Heycock, C. T., F.R.S.  
 Hinkel, L. E.  
 Hinks, E., M.B.E.  
 Hinks, Mrs. E.  
 Hoffert, Miss D. A.  
 Holleman, A. F.  
 Holleman, Mrs. A. F.  
 Horton, E.  
 Hunter, H.  
 Hutchinson, H. B.  
 Jackson, Sir Herbert, K.B.E., F.R.S.  
 Jackson, Lady.  
 James, T. Campbell.  
 Jeans, J. H., *Sec. R.S.*  
 Johnston, T. B., *Dean, Guy's Hospital Medical School.*  
 Kenyon, J.  
 King, H.  
 King, Mrs. H.  
 Kingston, Miss H. L.  
 Lakeman, Miss E.  
 Laker, J.  
 Lambert, B.  
 Le Pla, Miss M., *Indewer.*  
 Lessing, Dr. R.  
 Lessing, Mrs. R.  
 Leuchars, W. W., *Prime Warden, The Dyers' Company.*  
 Levy, Miss E. R.  
 Lowndes, J.  
 Lowry, T. M., C.B.E., F.R.S.  
 McBain, J. W., F.R.S.  
 McCombie, H., D.S.O., M.C.  
 Maclean, Mrs. I. S.  
 Maclean, H.  
 Macnab, W., C.B.E.  
 Manning, A. B.  
 Masson, I., M.B.E.  
 Meulen, H. ter.  
 Meulen, Mrs. H. ter.  
 Miall, S.  
 Miall, Mrs. S.  
 Micklethwait, Miss F. M. G., M.B.E.  
 Mitchell, A. D.  
 Mitchell, Mrs. A. D.  
 Monier-Williams, G. W., O.B.E., M.C.  
 Moody, Mrs. G. T.  
 Moore, T. S.  
 Moore, Mrs. T. S.  
 Morgan, G. T., O.B.E., F.R.S.  
*Morning Post.*  
 Morrell, G. F.  
 Morrell, Mrs. G. F.  
 Morris, H. J.  
 Mott, B., *President, The Institution of Civil Engineers.*  
 Newton, A. U.  
 Neilsen, H.  
 Neilsen, Mrs. H.  
 Nuthall, Tallant.  
 Ormandy, W. R.  
 Ormandy, Mrs. W. R.



- Orton, K. J. P., F.R.S.  
 Paget, H.  
 Paget, Mrs. H.  
 Palmer, W. G.  
 Palmer, Mrs. W. G.  
 Pedersen, Kai.  
 Perkin, W. H., F.R.S., *Past-President*.  
 Philip, J. C., O.B.E., F.R.S.  
 Philip, Mrs. J. C.  
 Pickles, S. S.  
 Plimmer, R. H. A.  
 Pope, Sir William J., K.B.E., F.R.S.,  
*Past-President*.  
 Porritt, B. D.  
 Pratt, W. R.  
 Pratt, Mrs. W. R.  
 Press Association.  
 Price, T. Slater, O.B.E., F.R.S.,  
*Secretary*.  
 Price, Mrs. T. Slater.  
 Pringle, Sir John, C.B.  
 Pyman, F. L., F.R.S.  
 Pyman, Mrs. F. L.  
 Raven, Sir Vincent, K.B.E., *President*,  
*The Institution of Mechanical Engineers*.  
 Reid, R. B., *President*, *The Institute of Brewing*.  
 Roberts, E.  
 Robertson, Mrs. E. G.  
 Robertson, Sir Robert, K.B.E.,  
 F.R.S.  
 Robertson, Lady.  
 Rogers, H.  
 Rosedale, J. L.  
 Rowlands, M. J.  
 Russell, A. S.  
 Sargeant, F. Pilkington, *President*,  
*The Pharmaceutical Society*.  
 Scott, A., F.R.S., *Past-President*.  
 Scott, Mrs. A.  
 Sharp, T. M.  
 Sharp, Mrs. T. M.  
 Sidgwick, N. V., F.R.S.  
 Simonsen, J. L.  
 Simonsen, Mrs. J. L.  
 Simpson, G. C., C.B.E., F.R.S.  
 Simpson, Mrs. G. C.  
 Smith, C., *Editor*.  
 Smith, Miss M. L.  
 Smith, T. B.  
 Spielmann, P. E.  
 Stern, A. L.  
 Stern, Mrs. A. L.  
 Stubbs, G., C.B.E.  
 Stubbs, Mrs. G.  
 Sugden, S.  
 Taylor, Miss M.  
 Thomas, R. N. Garrod.  
 Thomson, J. Millar, F.R.S.  
 Thorpe, J. F., C.B.E., F.R.S.,  
*Treasurer*.  
 Thorpe, Mrs. J. F.  
*Times*.  
 Tinkler, C. K.  
 Tinkler, Mrs. C. K.  
 Tryhorn, F. G.  
 Tryhorn, Mrs. F. G.  
 Turner, E. E.  
 Turner, Miss E. G.  
 Turner, G. W.  
 Turner, T., *President*, *The Institute of Metals*.  
 Voelcker, E.  
 Voelcker, E. W.  
 Voelcker, J. A.  
 Whiteley, Miss M. A., O.B.E.  
 Widdows, Miss S. T.  
 Woolcock, W. J. U., C.B.E., *President*,  
*The Society of Chemical Industry*.  
 Wynne, Miss D. P.  
 Wynne, W. P., F.R.S., *Past-President*.

After the loyal toasts had been honoured the President announced that he had had a telegram from Professors Bilmann, Bjerrum, Bohr, Brönsted, and Sørensen sending their hearty greetings and congratulations to the Society. This was received with acclamation.

The following is a list of the Toasts proposed :—

1. "His Most Gracious Majesty The King."
2. "Their Majesties the Queen and Queen Alexandra, His Royal Highness the Prince of Wales, and the other members of the Royal Family."

By Sir H. FRANK HEATH, K.C.B., Secretary of the Department of Scientific and Industrial Research :—

3. "The Chemical Society," coupled with the name of the President.

By Professor HENRY E. ARMSTRONG, LL.D., F.R.S., Past-President :—

4. "The Retiring President, Professor W. P. Wynne, D.Sc., F.R.S."

By Professor IRVINE MASSON, M.B.E., D.Sc. :—

5. "The Federated Societies," coupled with the name of W. J. U. Woolcock, Esq., C.B.E., President of the Society of Chemical Industry.

By Professor F. G. DONNAN, C.B.E., D.Sc., F.R.S., Foreign Secretary :—

6. "The Guests," coupled with the names of Professor Ernst Cohen, of Utrecht University (representing the Nederlandsche Chemische Vereeniging), and J. Hunter Gray, Esq., K.C., M.A.

Sir H. FRANK HEATH, K.C.B., in proposing the toast of "The Chemical Society," said :—

Mr. President, Ladies and Gentlemen, after I had accepted with some hesitation the invitation to address you this evening, and to propose this toast, I happened to be present at a public dinner where one of His Majesty's Judges said that after considerable experience of speeches of the kind he had come to the conclusion that most proposers of toasts began by explaining how unfitted they were for the task entrusted to them, and spent the rest of the time in proving it. Well, Ladies and Gentlemen, after that opinion from the Bench, there is nothing left for me but to throw myself on the mercy of the court.

I do, indeed, feel it to be a very great honour that a great scientific society like this should ask to have the principal toast of the evening proposed by a layman. You are not only a focus of research in pure science, you not only have a membership of 4,000 Fellows, but I see at these tables to-night inorganic and organic chemists, analytical and physical chemists, and not least of all, perhaps, biochemists. I won't suggest that the specialisation which is obviously taking place in your ranks has gone quite as far as the young American medical student of whom Dr. Howe told us in Philadelphia last autumn, who announced his intention of specialising in the ear, but had not made up his mind whether it was to be the right ear or the left. But specialisation there certainly is. Indeed, the foundation of the Society was an act of specialisation in 1841; when the Royal Society was first founded, I find from those

interesting records in *Nature* that the discussions ranged quite easily from naval architecture to the distillation of charcoal, from the anatomy of animal intestines to the discussion of a new digester for the brewing industry. Well, every one of those fields now has its own special society or societies. Specialisation must continue, I imagine, and increase, and yet to me as a layman I think there seems to be a movement in progress which must tend to counteract any disadvantages there might be from excessive specialisation; I mean the obvious tendency for different sciences to co-operate in the solution of the more difficult problems that are in front of you.

Professor Wynne, in his address this afternoon, referred to the Department with which I happen to be connected, and spoke of the share which chemists had undoubtedly had in the movement that led to the establishment of that Department. But I do not think that even you perhaps fully realise how close the link always has been, and I imagine always must be, between any organisation established to encourage scientific research and the chemists. Just look back. Professor Wynne's address was partly concerned in dealing with the review that Professor Meldola took before the war—I think in 1907—of the difficulties of the research worker in this country. Professor Meldola, a Past-President of this Society, was an original member of the Advisory Council of the Department of Scientific and Industrial Research and remained a member of that Council until his unfortunate death. Your new President, Dr. Crossley, is Director of Research to the largest Research Association for Industry that has come into existence since those difficult days of the war, the British Cotton Research Association, and that Association and Dr. Crossley are working in constant and continuous co-operation with the Department. Dr. Slater Price, another officer of this Society, is Director of the British Photographic Research Association; Sir Herbert Jackson, a former Vice-President, is Director of the Scientific Instrument Research Association; Dr. Pickard, a former member of your Council, is Director of the Leather Association; Dr. Scott, a Past-President, is a Director of the Laboratory established by the Department at the British Museum in order to study the best means of preserving antique objects of every kind; and finally there is your Treasurer, Professor Jocelyn Thorpe, who is to-day a member of the Chemistry Research Board of the Department and a member of many of its committees.

Now, my contact with all those distinguished men has made a double impression upon my mind. One is the adaptability of the chemist, and the other is his extraordinary power of penetration. Looking at the Research Association movement which I have

referred to already—incidentally there are twenty-four different industries which have organisations of this kind in this country, and the majority of the Directors of Research of those twenty-four Associations are chemists—I draw the conclusion that they must have great adaptability, because I happen to know that in many cases, and in some of the most outstanding cases, the chemists who have been called to those important posts knew nothing about the industry when they took up the appointment, and for that very reason have brought success. Professor Wynne told you this afternoon that those Associations have been useful because they have opened new posts to young men, and nothing could be more important than that. But I think he might possibly have added that these Associations have done more than that. I will tell you an experience of mine which explains. The other day I was in the largest textile mill in the world, and found that they have quite a large and busy research laboratory, and I was told that the reason that that laboratory had been established was because they had been so convinced of the value of research by the Association of which the firm was a member that they were determined to carry the matter further and have an organisation of their own within the works. That is going on all over the country; so that it is not merely if you look at it simply from the point of view of openings for young men—which after all is not the whole story—it is not merely that the Associations provide openings, but that in increasing measure the firms in the Associations as they come to realise the value of research will need the help of chemists and other men of science. And, sir, their power of permeation! Chemistry, it seems to me, has made its way already into almost every sphere of human life. You dictate to us, sir, what we are to eat, though I believe you are not entirely agreed as to the preservatives that should be used for our food; you give us new textiles to wear—or at least you give our wives new textiles to wear, and when we are ill you indicate to us, attracted as we are by the skilful advertisements of people who are out for that weakness of man that comes with illness, and you tell us where the medicines we are advised to take fail to come up to what they claim to be.

Now, sir, I could quite safely, with considerable safety, go on to tell you of the records of your great men who have been officers and Fellows of this Society. I could refer to the Central Library which you have established, which helps all the Societies connected with chemistry to have a nodal point from which they can gather their recorded information. I could speak of your research fund. I could tell you of the brave efforts you are making in spite of rising prices and a printers' strike to keep the publications going. But

if I did, I should only be telling you what you know far better than I do.

I am going to venture, sir, in view of the most excellent hospitality which you have offered me, and in view of the patience with which you, ladies and gentlemen, have listened to me up to the moment, I am going to venture to be bold, and to tell you how the present state of chemistry strikes a rank outsider.

I remember that when my brother-in-law, more than forty years ago, tried to teach me some chemistry, the molecule seemed to me a much more important thing than the atom. The atom, to my untutored mind, seemed a sort of axiom which you had to accept, but which compared with the interest of the molecule was a poor thing. Now I venture to think that possibly until comparatively recent times chemistry has concerned itself a good deal more with the molecule and its behaviour than with the atom. But is that condition going to last? The other night I heard a distinguished young biologist speaking of several sciences and claim as his belief that the central science of the future would be biology. He was prepared to take off his hat to physics and chemistry as important fundamentally, but the future lay with biology. One did not live in the cellars of a house, but in the upper storey. Well, as an outsider I am bound to say that I doubt that. To me, at any rate, and possibly to other people who are not chemists, chemistry seems to be taking increasingly a central position and bringing to its service the work, the tools, which other scientists on both sides of it are preparing. What has physics done recently from the point of view of chemistry? Has it not, by giving you the anatomy of the atom, and by revealing the structure of the space lattice, helped you to get a picture of three things—first, the mystery of chemical attraction, secondly, as Sir William Hardy, in his Bakerian lecture, pointed out, the phenomena presented by liquid and solid surfaces in close contact, and thirdly, the problem of catalysis. Those things are giving you, are they not, larger control over the speed and nature of reaction? But the engineer similarly is bringing in the tool of high pressure, and what will happen when the knowledge you already have, and these tools you already have, are brought to bear under the conditions of high pressure, it is very difficult to prophesy. And so you are forcing your way into the biological field. Another tool I fancy I see in your hands will be those mysterious accessory vitamins which link up your chemical work with those mysterious chemical reactions of the animal and vegetable organisms.

Well, sir, I have proved my incapacity for proposing this toast, and I will therefore ask you to drink to the health and future of the

Chemical Society, coupling with the toast the name of your President, Dr. Crossley.

Dr. ARTHUR W. CROSSLEY replied :—

I am sure the Society would wish me to thank you, Sir Frank Heath, very warmly for the way in which you have proposed this toast. My predecessor in this Chair has this afternoon answered, I think, fairly fully some of the remarks which you have made. He has expressed his appreciation of the efforts of the Department of Scientific and Industrial Research. Perhaps, as being somewhat intimately associated with that Department, I may be allowed to add one or two words. So far as my experience goes that Department is free from, shall we say, a Government monopoly—Red Tape, and is willing in every way possible to help anyone interested in the work it is doing. I have had some experience of the professional or professorial side of chemistry, and for the past five years I have had some experience of chemistry as applied to industry. I say, with full consideration of what I am saying, that in my opinion the Department has founded in the Industrial Research Associations a movement which is destined to play an all-important part in the future of this country. By no other means that I can conceive could science have been brought into those industries. I hope on some future occasion to speak somewhat more fully on this subject, and for the present, if you will not think it impertinent on my part, I should like to congratulate the Department on the big efforts which it has started and to say, "Don't be in the least discouraged by disparaging remarks that may be made about you."

I believe it is customary for the President on these occasions to make some reference to the affairs of the Society. This afternoon we had our Annual General Meeting, and by virtue of a decision arrived at, I find things weighing somewhat heavily on my shoulders. I refer to the decision which permits me to have the honour to occupy the position which I do at the present moment.

The election of one President, of necessity, means the retirement of someone who has occupied that post. It falls to more eloquent lips than mine to propose the toast of Professor Wynne this evening. I hope, however, that Professor Armstrong will forgive me if I say one or two words. When the time comes for Professor Wynne to apply for armorial bearings I would like to suggest that he take one single word for his motto, and that word is "Thorough." His sole aim has been efficiency, and in endeavouring to attain it he has not spared himself in the slightest degree. Few realise when he comes to a meeting and quietly says, "I think we should be well advised to do so and so," that this has possibly meant hours of thought, perhaps wrestling with the mystic language of charters and bye-

laws, perhaps the writing of numerous letters and documents. To do the right thing for the Society's welfare has been his sole object. I should like to speak on behalf of us all just one or two words to Professor Wynne. They are simple, but my long-standing friendship with him enables me to know, I think, that he will understand.

"Professor Wynne, we have learned to know something of the time, care and thought which you have expended on our behalf during the past two years. We appreciate; we are grateful."

The Chemical Society is rightly, in the opinion of its Fellows, a very exceptional and uncommon institution, indeed our forbears taught us to regard it as such. They did not found the Chemical Society of London, or England, or of Great Britain, they founded simply "the Chemical Society," and as such we are proud to regard it. We desire no addition: we ourselves are content to be chemists, without the added epithet of druggists which so many kind friends attempt to hurl at us. But I regret to say that when one consideration is taken into account we become quite unexceptional, quite common, and resemble most other societies, institutions, and individuals, inasmuch as we are finding it very difficult to make our income balance our expenditure. Up to the early days of 1914 we were quite a happy band, able to publish the original communications sent in by our Fellows, able to give our Fellows full value for their subscriptions and able to put by a small sum of money each year. In those days a page of the Journal cost 17s. 5d.; in 1921 the price had risen to £2 12s. 4d. It is true that at the present moment the price has fallen somewhat, but it is still well above twice the amount that it was in 1914. Moreover, the original communications are always on the increase, and we have now to make annual provision for the publication of 3,500 to 4,000 pages of Transactions alone. The situation is a very serious one from the point of view of the Society and it has given the Council furiously to think as to the possibilities of meeting it. The first step was to increase the subscription of our Fellows by 50 per cent. It is greatly to be regretted that it was found necessary to do so, for the majority of our Fellows are young men, and young chemists—in fact, I think I may say most chemists—are not over-burdened with this world's goods. The second step was to adopt the suggestion of the Treasurer to ask our Fellows to subscribe to a Publications Fund, the interest on which should be devoted to the upkeep of the Journal. We have raised in this way nearly two thousand pounds, but that is not enough, and we were faced this year with a possible adverse balance of some three thousand pounds. The Treasurer this afternoon told us we actually had a credit balance of some £210, but how has this been obtained? By ruthlessly cutting down the original communications

sent in for publication, to such an extent as to cause endless displeasure to authors and to leave it doubtful as to whether we are doing justice to their work; further, by asking Fellows to pay for the Annual Reports, which so far have always been distributed free, and by many other curtailments of our legitimate activities which, in my opinion, are greatly to the disadvantage of our Fellows and form a distinct danger to the prestige of British chemistry. Most societies, most institutions and most individuals themselves decide the pace at which they will live, and the pace is generally regulated by monetary possibilities. But the Chemical Society is again exceptional. The pace at which we are living has not been decided upon by ourselves, but has been decided upon by no less an authority than the nation.

I have stated that up to 1914 we were a happy band. In that year the nation spoke to us for the first time on record, I believe, but it spoke in no uncertain voice. It said, in the first place, "We are at war. We want certain drugs used for the alleviation of pain and suffering; we have so far obtained these supplies from abroad, and that source is now cut off. We are aware that these drugs have never previously been made in this country; we are aware that they require skilled labour for their production. Therefore we want you to prepare them for us." Well, those drugs were prepared by an organised effort on the part of the chemists of practically all the Universities and University Colleges in this country. Then came a second call. The nation said, "We want more explosives: T.N.T., picric acid, ammonium nitrate; we want acetone and dye-stuffs." Finally, there came a third call: "We want poison gas, poisonous and always more poisonous, and with each gas we want complete protection." I do not think it can be said that any of these calls were made in vain, or that the chemists of this country were found wanting in any way. So far as I know the chemists of this country, that is, the Chemical Society has never spoken back to the nation, but I suggest the time has come when this might be done, and in terms such as these:—

"In 1914 you asked us to do certain work for you, which we did to the best of our ability. We at once admit that some of our results were not forthcoming as speedily as we could have wished and in circumstances where speed was all important, due to the fact that the type of work which you asked us to do was new to us and we had perforce to gain experience. This experience has shown us clearly that in order to be prepared for any call which you may make upon us in the future, when delay may prove fatal, it is necessary that nothing should be left to chance, and it is therefore essential for us to carry out numberless researches so as to keep ourselves fully



informed of the possibilities of chemistry generally. Your requests of 1914 have greatly stimulated research activities in this country, and the publication of the increased number of papers has become a very serious matter to the Chemical Society, which can only meet the present situation by greatly curtailing its legitimate and rightful activities. In these special circumstances, will you not help us to carry on our legitimate work?"

I cannot think that such an appeal could possibly fall on deaf ears, for this very simple reason, that the Chemical Society through the efforts of its members has proved itself to be a national asset of the utmost magnitude and importance. Sir Frank Heath, once more I thank you for the way in which you have proposed the toast of the Chemical Society.

PROFESSOR HENRY E. ARMSTRONG (Past-President), in proposing "The Retiring President," Professor W. P. Wynne, said:—

Mr. President and Fellows of the Chemical Society, I ask you to lend me your ears and I hope I shall reach them. You have an unusual opportunity, an unusual spectacle, to offer to our guests to-night—that of a retiring President. The programme is wrongly printed. The "The" should be in Clarendon and "retiring" in italics. Presidents are not often retiring. Their business is to be unashamed and aggressive on behalf of the bodies they represent. A little more than two years ago I undertook two tasks: one, an easy one, was to convince the Society, the Council of your Society, that a particular person was *the* man for the office of President; the other, an almost impossible one, to cajole, to persuade, all but to force that particular person to recognise, as the walrus said, that his time was come to take on the many things pertaining to the President's office in our honourable body. It is little short of forty years ago, on March 27th, 1886, that he came to me as private assistant and had we been wise we should never have parted company. The years we worked together were the happiest and most fruitful of my life. We were not called upon to concentrate hydrogen ions; we never wasted time on noughts and crosses; no Lowry worried us with perpetual rechristenings of the already fully-named; we just quietly kept company with a hydrocarbon which was thoroughly well behaved and responsive. Our work was straightforward. There was no angle worship about it and we reported our results without fuss of any kind, in the briefest possible manner.

We put up ten signposts for the Di- and fourteen for the Trichloronaphthalenes and thereby demonstrated the truth of a doctrine fitly to be called, a *theory* of benzenoid structure, which I venture to say no X-ray analysis can upset. I think I may say

we were both proud of our exhibit at Wembley last year, when we thought of its implications. Our work pleased the Germans but it met with no recognition at home. It was unnoticed and that was a double compliment. It cost much toil during many years and a good deal of hard cash; neither of us made a halfpenny out of it.

I am told that Mr. Wells asks a couple of hundred pounds for a couple of thousand words. At all times, we could get what we wanted, what material we wanted, free of cost from Germany. We were never offered anything from our English works and our advice and assistance was never invited, although we worked in a technical college. Now, a great branch of the dye-stuff industry stands upon the foundation we built up. Yet neither before nor during the war, nor since, have we been asked to advise or assist in any way in the construction of the English edifice. Now, I modestly mention these points, in support of what the President said to-day as to the lack of co-operation between science and industry. When that address of his is printed, I trust that the measured terms in which he spoke on that subject will have their effect. I may say that the work was done in a sense *sub-rosa*, without official encouragement. I recollect on one occasion speaking to our hon. secretary, Sir John Watney, about research. His immediate reply was, "Your business is to teach boys, not to do research." That is the kind of encouragement we got in those days. This is the spirit that has been behind the comparative failure of our institutions to do original work, of which the President spoke to-day. It was not the primary fault of those who were working in the institutions.

I was glad to hear him speak out particularly on one subject—I think it was the keynote of his address—and say plainly that it is absurd for the Universities of this country all to attempt to do the same thing and on the same scale. Sir Frank Heath has told you of the tendency there is to specialise. A great lesson to be learnt by the Universities in this country is that they too must specialise. His University has no right to deal with anything but iron and steel and things of that kind. It will only be by specialising, that it will be possible for the several universities to effect the exchange of workers of which he spoke. Supposing we were to legislate to-morrow in the direction in which he spoke, all the research workers would drift to one or two places. That is a serious danger of any attempt of that kind.

Now to return to the man. My respect for his great ability as a worker, as a chemist and teacher and for the nobility of his character, has steadily increased with years. As a chemist, I

know of no better worker and teacher; as a man I have known no man so conscientious and self-sacrificing. I would recall to you the service he rendered as Editor in years gone by, of which our President gave so striking an illustration to-day. I wish the spirit he showed on that occasion could be manifest throughout the Society and I wish that Editors could be brought to take the same interest and at the same time show the same ability in their Editorial work that our late President displayed. You have heard how conscientious he has been. He has attended every possible meeting of the Society it has been possible for him to attend and he has done a great deal of outside work. Such a man deserves our thanks, not only for the work he has done, for the direct service he has rendered, more particularly must we thank him for the example he has set. Unsparring unselfishness is scarcely a present failing of the chemist, but the time is at hand when it must be your distinct characteristic.

Sir Frank Heath has rightly told you that after all it is not the atom but the molecule that is the real thing. The atom has no character until it joins up into the molecule. Speaking before the Institute of Chemistry recently, I said that chemists have reason to be proud of themselves on account of their achievements. At all events, the young women of the day are clad in cellulose and fine raiment mainly through your services. Even the Medical Research Council is faintly yearning for chemical aid. Sir Frank Heath spoke of Biology being the science of the future. Biology is nothing but chemistry when it comes to the real thing. Biology is making slow progress at the present time but most of the Bio-chemists, as I have said, are but bits of chemists. When they become chemists, there will be a real advance in vital chemistry and in medicine too. Still, with all this service to your score you have no recognised public standard and what is worse, no internal cohesion but lots of friction. You are not three hydrocarbons but more than thirty. Now is the time for you to show that you can come together, hold together, log roll together and organise together. There must be complete fusion of interests, I hold; an end must be put to the present chaos and inefficiency of publication. If necessary, to find funds, you must give up smoking. Your analyses will be more trustworthy if you do. There will be less tendency to believe in the transmutation of copper into lithium. No small temporary scheme will suffice. To be at all, you must be big.

Now, gentlemen, if you have any element of human feeling, you will sympathise with me in my determination to overcome to-night the modesty of your too-retiring President and join with

me in thanking him, with all possible warmth, for the distinguished way in which he has served the Society during the past two years and for the great example he has set by his unselfish devotion to the interests of our profession. I call upon you to join with me in drinking the future health and happiness of our late President, Professor Wynne.

Professor W. P. WYNNE, D.Sc., F.R.S., responding, said :—

I rise to thank you most heartily for the cordial way in which you have received the toast. I hope I may be allowed to regard it not as applying only to myself, but as including all those who have worked with me in the interests of the Society during the past two years. But for the loyal co-operation and cordial support of the officers, the Council and the office staff I could have done little or nothing, despite all the kind things Professor Armstrong has said in proposing the toast. He is my father in chemistry, and his eulogy is to be explained not by my merit but by the partiality often displayed by a parent.

As a father, Professor Armstrong is doubly fortunate, for, in addition to four distinguished sons who bear his name, he has a numerous chemical family of which I am proud to be the eldest. Two others of us, Sir William Pope and Professor Lowry, are also present this evening. As will have been gathered from what he said we may not be in complete agreement with our father's views on every subject—a not uncommon experience in families, chemical or otherwise—but that does not diminish in the slightest degree our affection for him or sincere appreciation of our fortunate upbringing.

Professor Armstrong referred to the date on which I became his private assistant. I had left South Kensington a few months earlier, and it was through Professor Japp's kind offices that this most happy chance came my way. If a reference may be permitted to the plea put forward this afternoon for the encouragement of migration, this crossing of Exhibition Road from the one College to the other did undoubtedly exercise a profound influence on my own career.

I had the good fortune to number among my teachers no fewer than seven Fellows of the Royal Society, five of them being Past-Presidents of this Society, and, on an occasion such as this, it is no less a pleasure than a duty gratefully to acknowledge my deep indebtedness to them. The first of these Fellows was Dr. George Gore, who, it may be remembered, published so long ago as 1865 an account of the modification in the properties of some seventy substances produced by complete desiccation, and thus was a pioneer in the field of research so closely associated with Professor

Brereton Baker's name. He was a self-made man. How he came to be chemistry master in King Edward's School, Birmingham, I do not know, but he had never been to a training college, and thus his originality had not been educated out of him. His method of judging the nature of our work was to suggest at the commencement of the class, that we should write a résumé of the previous lesson. This was assessed by the number of pages handed in at the end of a quarter of an hour, irrespective of the fact that some of them might contain six words and some of them sixty. That is the way in which I started to learn chemistry. Then, having left school, I went to evening classes after the day's work, and am a product of that system of "payment by results," under which science classes were farmed out to teachers, who were paid by fees based on successes achieved by their students in the examinations conducted by the Science and Art Department of those days. Despite the hard things which have been said about it, I do not think the system was wholly bad. At any rate it gave me my chance and to many others theirs. It provided, indeed, the only avenue to instruction in science subjects open to most students in the 'seventies of last century before University Colleges and Technical Schools came into existence. By its aid I went to South Kensington in 1881 and there had the great advantage of being a student under Sir Edward Frankland, Professor Percy Frankland and Professor Japp, who began my training in research. Thereafter followed the training as a teacher under Professor Armstrong, who taught me—nay, compelled me—to think; Sir Edward Thorpe, who brought me back to the old College, and Sir William Tilden, who last year, although in infirm health, did me the great honour of coming to the anniversary meeting and saying words which I shall never forget. I am to see him tomorrow, and I hope I may take to him from this gathering a message of affectionate regard and esteem. (Cheers.)

There is just one remark I should like further to make. Sir Frank Heath spoke in most appreciative terms of chemists and of their adaptability, for which we thank him. But it is only right to remember that the indebtedness to which he referred is not wholly on one side. I think the signal success which has attended the work of Sir William McCormick and Sir Frank Heath, neither of them men of science, in producing the result known as the Department of Scientific and Industrial Research, serves to show that success in such enterprises comes not only from a knowledge of men and affairs, but in no small measure from a sympathy with, followed by an understanding of, the type of problem to be solved.

As the thirty-ninth President, no longer retiring but retired, I salute my friend and colleague, the fortieth President, wishing him

as happy a time during his period of office as fell to my lot. Once again I thank you all most sincerely for the way in which the toast has been received. I do not deserve the praise; I have simply done my job.

The toast of "The Federated Societies" was given by Professor IRVINE MASSON, who said:—

There are, I suppose, few of us here who are so deeply learned in chemical politics as to be at once aware of what this term connotes; and I will therefore first adopt the old-fashioned plan of giving instruction by means of enumeration. The Chemical Society is affiliated with no fewer than seventeen others. Of the eighteen, four deal primarily with pure science—the Mineralogical, Faraday, Biochemical, and ourselves; twelve with the methods and the discoveries of pure science as applied to practical arts, namely the Society of Chemical Industry, Society of Public Analysts, Royal Agricultural Society, Institute of Brewing, Society of Dyers and Colourists, Society of Leather Trades' Chemists, Royal Photographic Society, Institute of Metals, Iron and Steel Institute, Ceramic Society, Society of Glass Technologists, Institution of Gas Engineers; and two are of a special character, namely, the Institute of Chemistry and the Association of British Chemical Manufacturers, which deal with chemists professionally and in their relation to the lay public.

What is especially made prominent by this list is, not so much the subdivision of pure chemistry, as the great number of ways in which the science as a whole has found a place in the business concerns of the nation. So evident is this, indeed, to chemists, that we have now and then to remind ourselves that if we have won the privilege of helping a little in the material welfare of our country, we cannot evade the responsibility which has thereby been entrusted to us. And, with this in view, the more we can do to foster intellectual sympathy between all kinds of chemists, the more will our science be able to serve the nation at large. And this is why there is a Federation of all these societies: it is a federation primarily *pro bono publico*, not merely *pro bono chemico*.

Let me indicate briefly two or three ways in which co-operation has usefully shown itself at present.

The Library of the Chemical Society has of late years been extended and is annually increased, with the set purpose of being useful not alone to its own Fellows but also to members of the other affiliated societies. Towards the heavy annual cost of this addition to its original function, many of these Societies have contributed; and now our Library, poorly housed though it is, is becoming a truly national asset. Last year, for instance, the

visits to consult our 30,000 volumes averaged about twenty-two per day; and of these, one-third of the consultations were made by members, not of the Chemical Society, but of other societies, while among the other two-thirds many were members of the Chemical Society and the others as well.

Another example is seen in the co-operation between the Chemical Society and the Society of Chemical Industry which has set going the Bureau of Chemical Abstracts. The Bureau has done a great deal of quiet work already, and it has before it the central problem of unifying the British publications which survey each month or fortnight the whole of the world's current literature of chemistry. Surely no obstacle short of insuperable bankruptcy should be allowed to stand in the way of an end so desirable.

A collective token of federation is, I take it, to be seen in that body of delegates, the Federal Council for Pure and Applied Chemistry. There is something in this Council which reminds one of the luminiferous ether. It was originally invented to offer a medium for the propagation of light and radiation of energy, and to overcome the difficulty of action at a distance. Yet, I have been told, experiments made with the object of detecting it in motion have failed; and some daring moderns have even questioned the necessity for believing in it, and have dubbed it a pure convention.

Now there is a name which I have to couple with this toast—that of Mr. Woolcock. Chemists, as such, are trained to deal with things which are in themselves non-human; yet, because these things, and we ourselves, must everywhere affect human affairs, we need human guidance. It is to wise and experienced men like Mr. Woolcock that we instinctively turn for such help; and not one of you does not know how well and generously Mr. Woolcock gives it—think of one example alone, chemistry at Wembley. Mr. Woolcock fulfils the function of an ideal catalyser; for he starts, facilitates, or hastens actions, without upsetting any equilibrium, and himself emerges apparently unchanged at the end.

I ask you to couple with the toast of the Federated Societies the name of Mr. Woolcock.

Mr. W. J. U. WOOLCOCK in his reply stated :—

I feel my efforts to respond to this toast will be somewhat inadequate, the more so as on looking at the toast list and seeing the term, "The Federated Societies," I did not know what was meant by it. My chemical education is, as you know, very limited. Hitherto I have supposed that I knew just sufficient chemistry to understand what the real chemist was talking about when I had to take his advice. For once I have failed. Professor Masson, convincing as

he is on most subjects, lucid to a fault on his own particular subject, has left me absolutely in the dark as to what is meant by the "Federated Societies." I at first thought that possibly it was a misprint and that Sir William Pope was intended to reply on behalf of the Federal Council. The delightful language in which Professor Masson brushed on one side the Federal Council leaves me in no doubt that he is not referring to that body, but he gave us, in order that we might know exactly about what we are talking, a list of learned bodies which, in the hope or in the anticipation of the Chemical Society, will ultimately become federated. Let us hope that that will eventuate. In future when I have to think of a reason why I should be considered a chemist, I shall always think of what Sir Frank Heath said, and regard adaptability as a qualification in a claim for that distinguished name, because I think it is a qualification which those of us who lack some qualification in science may readily embrace and regard as practicable, and in that way seek admission to the inner circle, because it is very true that the chemist is an adaptable person, and those who have to have something to do with him need to be adaptable as well.

It has been my fortune during the past twelve months to study two chemists at very close range. In fact, if I had attempted to define the Federated Societies I should have thought of a rather shorter list, and thought of the Chemical Society, the Institute of Chemistry and the Society of Chemical Industry, because of the real federation which has existed between those three bodies for some little time, and perhaps never more closely than during the past twelve months. I have been able to study at short range the Presidents of the Chemical Society and the Institute of Chemistry. We have travelled together, and it is a common thing for Professor Henderson and myself to speak together in different towns. That kind of intimacy brings familiarity and a working together which can only be obtained in that way. I remember that some time ago we arrived in Birmingham together. We had been in Glasgow the night before and had as usual said the proper thing about each other. Professor Henderson, when we got to Birmingham, called my attention to a placard just outside the station, and, after a quick glance, said, "They know we are coming," but not taking it quite as quickly as Professor Henderson, I saw that he was mistaken and I studied it a little more closely. The two Macs advertised there were not ourselves.

During the past twelve months there has been hardly a local branch of the Society of Chemical Industry or of the Institute of Chemistry that has not had a joint dinner. This indicates a desire for co-operation among the rank and file of which those who are



temporarily the leaders of the chemical societies and associations in this country will have to take notice.

I do not myself believe it is possible for the Councils of the various Societies to lay down a definite scheme for federation and to attempt to impose that on the local branches of the various Societies, but I do think that at the present time there is a demand throughout the country that we shall do something to prevent this appalling overlapping and duplication in the production of chemical literature, and do something which will satisfy the man who likes to consider himself in the rank and file and who at the same time feels that there is a definite need for a closer union among the Societies and the Associations.

Well now, neither Professor Wynne nor Professor Henderson nor myself is capable of doing that sort of thing individually. Together, of course, we have found it very easy. If we were upon a job which required modesty of demeanour, Professor Palmer Wynne did it. If it required some of that native shrewdness and ruggedness of character, Professor Wynne and I pushed Professor Henderson into it. If, of course, it were a mere torrent of words that was required, you know what would happen. But unlike the Duke of Plaza Toro, we have no desire to lead our Societies from behind, and in our individual capacity—not in our representative capacity—we have prepared a scheme for a Chemistry House to which each of us felt entitled to put his name, not binding our respective Societies or Associations in any way. This is a scheme which we feel we can recommend to those of our friends who are prepared to listen to our recommendations. I feel that with you, Dr. Crossley, in the chair in succession to Professor Palmer Wynne—and if I may say so, I welcome you very heartily in the chair—the work will continue.

We of the "Federated Societies," yes, of the Federated in inverted commas Societies, thank you very much indeed for inviting us to-night, and thank Professor Masson for proposing the toast. We wish the Chemical Society every prosperity during the coming year, and hope that the traditions which have been built up during the past four or five years of close working and co-operation between the officers of the various Societies will be maintained. We trust that under your guidance those traditions will continue and we may be even more successful in the coming year than in the past.

Professor F. G. DONNAN, C.B.E., D.Sc., F.R.S. (Foreign Secretary), proposed the toast of "The Guests," coupled with the names of Professor ERNST COHEN, of Utrecht University (representing the Nederlandsche Chemische Vereeniging), and Mr. J. HUNTER GRAY, K.C., M.A. \* He said :—

We have here to-night four distinguished representatives of

Holland, Professor H. J. Backer, Professor Ernst Cohen, Professor A. F. Holleman, and Professor H. ter Meulen. Three of them are accompanied by their wives. May I say that we wish these ladies also a very hearty welcome to London and to the Chemical Society dinner.

I believe it is true that although the population of Holland is relatively small, actually the largest number of Nobel prizes has been given to that nation, which is a wonderful tribute to the scientific output and ability of Holland. It is nothing new, for that country has always been perhaps the greatest centre of scientific culture in Europe. I have great pleasure in saying a few words about my friend Professor Cohen, of Utrecht, whose name I have the honour to couple with this toast. I think it is rather late in the evening to refer to the distinguished work of Professor Cohen, but he is the most eminent pupil of that great man, Professor J. H. van't Hoff, and is one of the greatest authorities on the effect of high pressure on chemical reactions, and many other things.

When I come to look at the list of other distinguished guests associated with this toast, I feel like a miserable sinner transported to Paradise and asked to propose the toast of all the holy Saints. The Rt. Hon. Sir John Anderson, G.C.B. (Permanent Under-Secretary of State for Home Affairs), is one of our guests, and may I assure him, speaking as one Secretary of State to another, that if in the conduct of the affairs of this great country he wishes for any advice, the President of the Chemical Society will be always willing to help.

I have also the pleasure of coupling with this toast another name, that of one of those modest men of law, Mr. J. Hunter Gray. I have had the honour to be associated with him in one or two cases. It is needless to speak about these great men, because we all spend our nights reading the *Evening Standard*, and our days reading *The Times*, and we have the greatest admiration for their work.

There is one thing I should like to say before I conclude, namely, in reference to a very important part of the toast, that of the ladies present to-night. We wish them all a very hearty welcome.

It is my great pleasure and honour now to give you the toast of "The Guests," coupled with the names of Professor Cohen and Mr. Hunter Gray.

Professor ERNST COHEN, who replied for the Dutch chemists present, said :—

During the toast of my friend Donnan I made some notes, but it seems to be impossible to make a response to all the remarks he made in the toast. I think it would take too much time. This afternoon I had a warning from the new President of your Society

that everyone must be brief. I think there is no nation more fond of conciseness in speech than the English. Take, for instance, your chemical abstracts. When an English chemist wants to describe the properties of any substance or fluid he says: B.P. 100, F.P. zero, D.C. 80, and for those who are not familiar with those telegraphic hieroglyphics I will add that B.P. means boiling point, F.P. freezing point, D.C. dielectric constant.

In English literature or poetry you find absolutely the same thing. I remember an English rhyme made up of initial letters which, for those who are not in a hurry, I will translate:

A fishy old fisher, called Fisher,  
Fished fish on the edge of a fissure.  
The fish with a grin  
Pulled the fisherman in.  
Now they're fishing for the Fisher within.

But the most striking conciseness is found in the language of English daily life. When I have to write a letter to the Foreign Secretary of the Chemical Society I write: F. G. Donnan, M.A., Ph.D., F.R.S., F.S.C.S., London, W.C.1, and so I could go on. If I were to follow these lines in responding, I would have to condense them into a few initials, which in plain English would mean, "I wish to the Council and the Fellows of the Chemical Society, good luck, welfare, prosperity and happiness."

Ladies and gentlemen, as I am a foreigner, you will allow me to express myself in a somewhat more elaborate way. In the first place, I have to thank the Council and the Fellows of the Chemical Society in the name of my Dutch colleagues who were so kindly invited to attend this dinner and the Annual Meeting this afternoon, and also to thank you in the name of the Dutch Chemical Society whose representatives are prevented from being here and celebrating with you the birthday of this Society with which so many illustrious names are linked.

There is a French saying which means, "Every meeting we finish by a dinner whenever we can, and it is by a dinner that we rule over man." But I make an alteration in the last line and say, "It is our dinners which delight ladies and men." The question arises as to the origin of the custom of finishing such a meeting with a dinner. We have had two dinners to-day; in the afternoon our President gave us mental food in his most interesting lecture, and now we have material food. Whence comes the custom of linking the two? It is your countryman, Joseph Priestley, to whom you are indebted for this most pleasant custom. Priestley has been pictured in a fascinating way in a caricature by one of your countrymen as sitting at a dinner, but at a dinner which he never attended.

Priestley was a very wise man. He also invented soda-water, a very good remedy for many persons who have attended a dinner. I have been so lucky as to find the caricature, and I have had it copied and will ask you all to accept a copy not only as a memento of this splendid invention by your countryman, but also as a memento of most pleasant hours spent in your company. I feel sure that my Dutch colleagues will feel with me that we have had a very interesting meeting and enjoyable dinner with you, and thank you all for the very kind way in which you have invited and entertained us.

Mr. J. HUNTER GRAY also replied, saying :—

Professor Donnan, and members of the Chemical Society, a few days ago I had the burden and privilege to make the last speech at another meeting and I had taken the greatest trouble to prepare an impromptu speech to deliver on that evening. It passed through my mind that I might palm it off once more, but I had no sooner come into this room than I found two members of this company—Sir Frank Heath and Professor Armstrong—who had heard my last impromptu effort. Therefore I am thankful I had made preparations for another impromptu speech.

This toast recalls to me a set of questions and answers which appeared recently in one of the newspapers. The publication of those questions and answers was for the purpose of demonstrating the super-excellence of a system of education in this country for which we paid so many millions of pounds annually. One question put was, What is a Guest? One bright youth answered, "A Guest is a joke." Well, I hope the guests are not worse than jokes to-night, because I would rather be a guest than a nuisance, especially as I am making the last speech on the toast list. The guest who talks too much is apt to become a nuisance, so I will be quite brief. Another answer was, "A Guest is a person usually of the male sex who eats and drinks as much as he can and pays nothing for it." I suspect that the young person who wrote that answer was a precocious member of the other sex. But we do, as guests, come within that definition.

We to-night are guests of a most eminent body of scientific men, and it is inevitable that our thoughts should be extraordinary when we hear about molecules and atoms and the somewhat dubious relationship between them, and we may play with unusual ideas. For example, usually when I look at the menu and note the various courses and I see there is one course entitled *Saumon d'Écosse* with some other French words, I should say that was good Scotch salmon. But no such thoughts came into my mind to-night. When I put my knife into that salmon, I wondered if I should find at least a dozen of those bodies Sir Frank Heath referred to, vitamins,

running about, and perhaps I might even find a few of those bodies known by some curious names, and see the poor little vitamin running away and calling in terror-stricken tones, "Yadil, Yadil."

But let me be serious. I am not one of those, although a mere lawyer, who think that the premier gifts of scientific genius have departed from this country. I believe that in the future, as in the past, our British men of science will remain in the van of scientific progress. The whole world has marvelled at the wonderful work done by them, and especially, may I say, by our chemists in the Great War, and believing, as I do, that any future warfare will depend more and more upon scientific progress, I have no fear, if only the public and the Governments of this country will give to science that encouragement which it demands and which it deserves.

I am proud to be associated with the great scientist Professor Cohen to-night in responding to the toast of the Guests. We, the Guests, thank you, our Host.

Ordinary Scientific Meeting, Thursday, April 2nd, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following :

Honorary Fellow.	Elected.	Died.
Guglielmo Körner .....	Jan. 20th, 1898.	March 28th.
Fellows.		
Charles Samuel Mummery .....	Dec. 5th, 1907.	March 27th.
Robert Atkinson Oddy .....	Feb. 21st, 1918.	March 12th.

The PRESIDENT announced :

1. That the Keith Gold Prize Medal of the Royal Society of Edinburgh awarded to the late Robert Traill Omond, LL.D., has been lent by Mr. Arnold Stevenson for exhibition in the Medal Case. It is hoped that other Fellows will add to the interest of the Society's Collection by loan or gift.

2. That the following Committees for 1925-1926 had been appointed by the Council :

Finance Committee : J. L. Baker, A. Chaston Chapman, F. P. Dunn, C. A. Hill, G. T. Moody, R. H. Pickard, and the Officers (Treasurer as Chairman).

House Committee : J. L. Baker, Sir Herbert Jackson, Alexander Scott, J. M. Thomson, Sir William Tilden, E. W. Voelcker, and the Officers.

Library Committee : P. P. Bedson, O. L. Brady, J. R. Partington (Chairman), Sir Thomas K. Rose, Alexander Scott, J. F.

Spencer, the Officers, and the Librarian, together with the following representatives of contributing Societies : J. L. Baker, R. B. Brown, J. C. Drummond, A. Harden, J. P. Longstaff, R. L. Mond, G. Senter.

Publication Committee : H. B. Baker, E. C. C. Baly, H. Bassett, O. L. Brady, H. W. Dudley, U. R. Evans, J. J. Fox, A. J. Greenaway, I. M. Heilbron, T. A. Henry, C. K. Ingold, H. McCombie, I. Masson, W. H. Mills, T. S. Moore, G. T. Morgan, J. R. Partington, J. C. Philip, R. H. Pickard, F. L. Pyman, N. V. Sidgwick (Chairman), W. P. Wynne, and the Officers.

Research Fund Committee : A. J. Allmand, H. B. Baker, E. C. C. Baly, J. B. Cohen, W. H. Mills, Sir Robert Robertson, R. Robinson, N. V. Sidgwick, Sir James Walker, W. P. Wynne, and the Officers.

The following were formally admitted Fellows of the Chemical Society : G. E. Gardam, G. E. Watts.

Certificates were read for the first time in favour of :

Neville Melton Bligh, A.R.C.S., A.I.C., 67, Castle Road, Bedford.

Hugh Alexander Millar Borland, M.Sc., A.R.C.S., 14, Cotham Road, Bristol.

Malcolm Sinclair Gaskill, 3, Buckingham Road, Hilton Park, Prestwich, Manchester.

Norman Hamer, Ash Mount, Holcombe, Manchester.

Ivor Gray Nixon, 75, The Vale, Golder's Green, N.W. 11.

Vincent Joseph Occleshaw, M.Sc., A.I.C., 22, Byrn Street, Ashton-in-Makerfield, Wigan.

Leon Rubenstein, B.Sc., 87, Eaton Grove, Swansea.

Alec Thomas Streather, B.Sc., A.I.C., 3, Wellington Road, Watford.

Violet Corona Gwynne Trew, 18, Adam Street, Portman Square, W. 1.

The following papers were read :

"The formation of *d*-2:2:4-trimethylcyclohexan-3-one-1-carboxylic acid from *d*-camphorquinone." By C. S. GIBSON and J. L. SIMONSEN.

"Aromatic esters of acylegonines." By W. H. GRAY.

"The decomposition of hydrogen peroxide by cobaltic hydroxide." By F. G. TRYHORN and G. JESSOP.

## RESEARCH FUND COMMITTEE.

A meeting of the Research Fund Committee will be held in June next. Applications for Grants, to be made on forms which can be obtained from the Assistant Secretary, Chemical Society, Burlington House, W. 1, must be received on or before Monday, June 1st, 1925.

All persons who received grants in June, 1924, or in June of

any previous year, whose accounts have not been declared closed by the Council, are reminded that reports must be returned by June 1st.

### PUBLICATIONS FUND.

In connection with the Appeal for the Publications Fund issued by the Treasurer, it has been decided that a list of donations and subscriptions received shall appear in the Proceedings for June. All donations and subscriptions received prior to the end of May will be included in the List.

### LIST OF FELLOWS, 1925.

It has been decided to print the List of Fellows for 1925 and to supply the List to those Fellows who make application to the Assistant Secretary by the 31st July, 1925.

### BERICHTE, 1915 to 1924.

Sets of the Berichte from 1915 to 1924 (10 years) are now offered to Fellows of the Society at £22, carriage extra. Application should be made to Mr. S. E. Carr.

List of Papers, or Abstracts thereof, received between March 20th and April 2nd, 1925. (This list does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"The thermal decomposition of ammonia upon various surfaces."

By C. N. HINSHELWOOD and R. E. BURK.

"Strychnine and brucine. Part III. The position of the methoxyl groups in brucine." By F. LIONS, W. H. PERKIN, and R. ROBINSON.

"Compounds of tervalent molybdenum. Part III. New oxalates." By W. WARDLAW and W. H. PARKER.

"The composition of starch iodide." By H. D. MURRAY.

"Note on the atomic volume of manganese." By A. N. CAMPBELL.

"Note on molybdenum semipentoxide." By W. WARDLAW and F. H. NICHOLLS.

"The action of hydrogen chloride on *cyclohexylideneazine* and on *cyclopentylideneazine*." By W. H. PERKIN and S. G. P. PLANT.

- "The constitution of soap solutions in the presence of electrolytes : sodium laurate and potassium chloride." By W. C. QUICK.
- "The tautomerism of dyads. Part III. The effect of the triple linking on the reactivity of neighbouring atoms." By E. H. INGOLD.
- "The molecular condition of phenol in benzene solution." By J. C. PHILIP and C. H. D. CLARK.
- "The solubility of sulphur dioxide in water and in aqueous solutions of potassium chloride and sodium sulphate." By J. C. HUDSON.

**CERTIFICATES OF CANDIDATES FOR ELECTION AT  
THE BALLOT TO BE HELD AT THE ORDINARY  
SCIENTIFIC MEETING ON THURSDAY, MAY 7TH, 1925.**

BJERRUM, NIELS JANNIKSEN, Copenhagen, Vendersgade 28. Danish. Professor in Chemistry at the Royal Veterinary and Agricultural College in Copenhagen. Researches on liquid potentials, on complex compounds, especially of chromium, on the ionisation of electrolytes, on the thermic dissociation of water and carbon dioxide, on the theory of titration, on the atomistic explication of ultra-red spectra, etc. (*Signed by*) F. G. Donnan, J. N. Collie, W. E. Garner.

BLUNSDEN, ARCHIBALD BERESFORD, "The Bungalow," Westbury-on-Trym, Bristol. English. Asst. Tech. and Analytical Chemist. Employed for over five years by The British Oil and Cake Mills, Ltd. (Bristol branch) in research, etc., in their laboratory and works. Evening study at the Merchant Venturers Tech. College, including lectures, advanced analysis, and research. City and Guilds of London Institute Final Certificate (Technological) in Oils, Fats, and Candle Manufacture. National Certificate in Chemistry. Desire to keep up-to-date with advance in the scientific world. (*Signed by*) Arthur Marsden, M. W. Jones, Chas. J. Waterfall, S. Siddons Wilson.

BLYDE, GEOFFREY ALGER, "East Cliffe," East Bank Road, Sheffield. British. Steel Maker at A. Blyde & Co., The Wallace Steel Works, Sheffield. Late Student of Metallurgy, Applied Science Department, The University of Sheffield. I am desirous of joining with a view to extending my knowledge of Chemistry and Metallurgy by the use of the Society's Library and Journals. (*Signed by*) John Evans, L. Archbutt, J. E. A. Blyde.

BOWLES, THOMAS HENRY, "Allandale," Meadowside Rd., Cheam, Surrey. British. Chemist, 1st Grade, Government Chemists' Department. 28 years Government Chemists' Department. (*Signed by*) R. Robertson, Geo. Stubbs, J. J. Fox.

BRINDLEY, WILLIAM HARRISON, 11, Millmoor Terrace, Glossop, Derbyshire. British. Demonstrator in Chemistry, Faculty of Technology, University of Manchester. M.C., M.A. (Cantab.), M.Sc.Tech. (Manc.), A.I.C. Demonstrator as above since 1921. Joint author of "An Attempt to Resolve Quaternary Phosphonium Compounds," and "Some Esters of Anisic Acid." (*Signed by*) Frank Lee Pyman, Fredk. M. Rowe, John K. Wood.

BUCHAN, JAMES LINDSAY, Hampden Club, London, N.W.1. British.



Physico-chemical Research Student, University College, London. B.Sc. (Lond.), Hons. Chemistry. (*Signed by*) F. G. Donnan, W. E. Garner, D. McKie.

BULL, FRANK HENRY CHARLES, 50, Cornwall Road, Bishopston, Bristol. British. Works Chemist in the employ of Bristol Gas Company, Bristol. B.Sc. degree 1916 (Bristol University) (Subjects: Chemistry, Physics, Mathematics); Associate of the Institute of Chemistry, 1919; Full Technological Certificates in Gas Engineering and Gas Supply from City and Guilds of London Institute, 1923—4. (*Signed by*) F. Francis, J. W. McBain, M. E. Laing.

BUTLER, JOHN ALFRED VALENTINE, "The Potteries," Winchcombe, Glos. British. Assistant Lecturer in Chemistry, University College of Swansea. M.Sc. (Birmingham), 1922. Author of papers: *Trans. Faraday Soc.*, 19, 659, 729, 734, 1924; *J. Phys. Chem.*, 28, 438, 1924; *Phil. Mag.*, 48, 746, 927; *Zeits. phys. Chem.*, 113, 279, etc. *J.C.S.*, 1923, pp. 2370, 2380; 1924, pp. 963, 1101 (jointly with other authors). (*Signed by*) G. T. Morgan, S. R. Carter, J. E. Coates, L. E. Hinkel, E. E. Ayling.

BYFORD, ANNIE LAVINIA, 73, Elderton Rd., Westcliff-on-sea, Essex. British. Student of Chemistry. B.Sc. (Pass). Studying for B.Sc. Honours in Chemistry at Bedford College for Women. (*Signed by*) J. F. Spencer, H. Crompton, P. V. McKie, E. R. Levy.

CLEGG, JAMES HERBERT, "West Cliffe," Queens Park Rd., Burnley. British. Engineer and Manager, Burnley Corporation Gas Dept. Member of the Institution of Gas Engineers. My object in seeking membership of your Society is to extend my knowledge of and assist in the furtherance of Chemical Science. (*Signed by*) Raymond Ross, Ernest Hardiker, J. P. Leather.

COCKROFT, HORACE CECIL, 6, Highfield Terrace, Halifax. British. Schoolmaster. London, B.Sc., 2nd Class Hons. Chemistry, 1922; Associate of the Institute of Chemistry, Jan. 1923; Student at University College, Reading, 1919—1922. Research work on  $\text{CuCN-KCN-H}_2\text{O}$  system incorporated in paper, Bassett and Corbett, *J.C.S.*, Vol. 125, 1924. (*Signed by*) Robt. D. Abell, H. Bassett, J. W. Dodgson.

COYNE, FRANCIS XAVIER, 160, Addison St., Blackburn, Lancs. English. Student at the Blackburn Technical College. Three years' work at a Manufacturing Chemist's as a chemist, in the laboratory. Proficiency in Chemistry, Physics, Mathematics, German, French, Latin, and Greek. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, Robert H. Pickard.

CRAIK, JAMES, The University, St. Andrews. British. Carnegie Research Fellow. M.A. 1920 (St. Andrews). B.Sc. 1921 (St. Andrews). Ph.D. 1924 (St. Andrews). Author of a paper entitled "The Mechanism of the Oxidation of Typical Carbohydrates with Hydrogen Peroxide and Hypochlorous Acid," *J. Soc. Chem. Ind.*, 1924, 43, 171. At present engaged in Research Work in the Chemistry Department, University of St. Andrews. (*Signed by*) J. C. Irvine, John Read, G. M'OWan.

DANE, HERBERT GREETHAM, The Diocesan Training College, Winchester, Hants. British. Tutor and Lecturer (and Demonstrator) in Chemistry at the Winchester Training College. B.Sc. with First Class Honours in Chemistry, Sheffield, 1922. M.Sc. (Sheffield) 1923. Worked under Dr. J. Kenner 1921—22 on the Influence of Steric Factors on Intramolecular Condensation, see J. Kenner and E. Witham, *T.*, 1921, 1452. (*Signed by*) W. P. Wynne, F. G. Tryhorn, Arthur W. Chapman.

DEAN, HARRY, 134, New Lane, Oswaldtwistle, nr. Accrington. English.

Textile Chemist and Colorist. Assoc. Manchester Coll. of Technology (Bleaching, Dyeing, and Printing, including advanced Organic Chem. and Dyestuffs Intermediates). 3rd year College Certificate of Blackburn Tech. Coll. (Inorg. and Organic Chem. and allied subjects). (*Signed by*) Percy J. Rhodes, G. W. F. Holroyd, E. Knecht.

DIXON, MARGARET STEDMAN LEONORA, Homebush, Worcester Rd., Sutton, Surrey. British. Student. A student taking a B.Sc. Honours Degree in Chemistry at Bedford College for Women (University of London). (*Signed by*) J. F. Spencer, H. Crompton, P. V. McKie.

FARNELL, ROBIN GEORGE WESTBURY, Exeter College, Oxford. British. Chemist to the British Empire Sugar Research Association, 3, 5, 7, Old Queen St., S.W. 1. A.R.C.S. A.I.C. Research into the colloidal constituents of the juice of the sugar cane. (*Signed by*) James C. Philip, M. A. Whiteley, H. B. Baker.

FAULKNER, IRVINE JOHN, Emmanuel College, Cambridge. British. Research Student. (*Signed by*) T. M. Lowry, R. G. W. Norrish, L. P. McHatton.

FLETT, THOMAS, Anchor Cottage, Kirkwall, Orkney. British. Chemist. At present Works Chemist in a Factory. 4 Years' Course at Glasgow University, 1919—1923; Graduated B.Sc. (Applied Chem.) and was elected A.I.C., 1923; Works chemist at Thornley Binders, Ltd., since January 1924. (*Signed by*) G. G. Henderson, T. S. Patterson, R. Wright, S. Horwood Tucker.

GARDNER, THOMAS JAMES ELIJAH, 12, Bushwood Road, Kew, Surrey. English. Works Chemist (Consol Products, Ltd., Sunbury Common, Middlesex). 30 Years' experience in Manufacturing Chemistry, especially in the investigation and perfecting of Synthetical Essences and like products. I am anxious to keep in touch with the developments of modern Chemistry, particularly as applying to my own work. (*Signed by*) Francis W. Hodges, Frank A. Boys, Archibald Macpherson.

GARRAN, RICHARD RANDOLPH, Orphir, St. George's Rd., Toorak, Melbourne, Australia. Research student at the University of Melbourne. Bachelor of Science (Melbourne), 1st class Honours and Exhibition in Chemistry in first and second years, 2nd class in third year. Has since done a year's research (heterogeneous equilibrium) and is at present reading for Final Honour Examinations in Chemistry. (*Signed by*) A. C. D. Rivett, E. J. Hartung, W. Davies.

GIBLIN, JOHN CHARLES, 3, Kensington Terrace, Brecon, Wales. British. Science-master, Christ College, Brecon. Bachelor of Science (London, 1st Hons. Chem.). Associate of the Institute of Chemistry. (*Signed by*) W. J. Jones, Claude M. Thompson, E. P. Perman.

GILCHRIST, HELEN SIMPSON, 82, North St., St. Andrews. British. Research Chemist, Food Investigation Board, D.S.I.R. B.Sc. (St. Andrews), 1917. Ph.D. (St. Andrews), 1921. Author of a thesis on "The Preparation and Constitution of Synthetic Fats, containing a Carbohydrate Residue." Assistant in Chemistry, The University, St. Andrews, 1918—21. Joint author, with Principal Irvine, of (1) A Synthetic Fat, etc., *T.*, 1924, 125, 1. (2) Condensation of Mannitol with Olive Oil, *ibid.*, 10. (*Signed by*) J. C. Irvine, John Read, G. M'OWan.

HADFIELD, ISABEL HODGSON, 65, Langham Rd., Teddington, Middlesex. English. Research Chemist. M.Sc., London University. Seven years' research work for the Aeronautics Advisory Committee. Member of the staff at National Physical Laboratory. (*Signed by*) Guy Barr, L. L. Bircumshaw, J. T. Hewitt.

HALPIN, JAMES FRANCIS, St. Chads, 39, Benson Road, Forest Hill, S.E. 23. British. Superintending Chemist, Government Chemist's Department. Superintending Chemist in the Government Laboratories. Fellow of the Institute of Chemistry. (*Signed by*) Robert Robertson, Geo. Stubbs, A. More, J. J. Fox.

HANSON, DONALD, 7, Willow Bank, Halifax. English. Works Chemist. Passed in Physics as subsidiary to taking Honours B.Sc. (External) of London University. Also 8 years' Laboratory and Technical Experience in Explosive Manufacture, Tar Distillation, Textile Chemistry, and Analytical Work. (*Signed by*) W. Sowden, G. C. Riley, W. J. Stansfield.

HAWORTH, THOMAS, 8, Park Terrace, Fielding Lane, Oswaldtwistle, Lancs. English. Assistant Gas Engineer and Manager, Oswaldtwistle Urban District Council. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

HEATON, JOHN STANLEY, 43, Birch Rd., Crumpsall, Manchester. British. Research Chemist. Student and research worker at Liverpool University for five years. B.Sc. (1st Hons.). Ph.D. Now engaged on research in textile industry. "The Investigation of Meso-thioanthracene Derivatives. Part I," Heilbron and Heaton, *J.C.S.*, 1923, 123, 173. (*Signed by*) I. M. Heilbron, William Doran, F. C. Guthrie.

HENSMAN, JOHN CYRIL, M.A., A.I.C., Aldenham School, Elstree, Herts. British. Chemistry Master, Aldenham School. 1921, Cambridge Natural Sciences Tripos, Part I (Chem., Physics, Physiology); 1923, Cambridge Natural Sciences Tripos, Part II (Chemistry); 1923, elected to an Associateship of the Institute of Chemistry; 1923-4, Asst. Science Master, Rotherham Grammar School, Yorks.; 1924, Chemistry Master, Aldenham School. (*Signed by*) T. M. Lowry, W. H. Mills, Charles T. Heycock.

HILL, JOSEPH, 58, Spring St., Accrington, Lancs. English. Chemist (Works). Past Blackburn Tech. College, 4th year Day Course. Occupation: Chemist, East Lancashire Soap Works. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

HOCKING, FREDERICK DENISON MAURICE, 18, Woodside Park Road, N. Finchley, N. 12. British. Biochemist (and at present Final Year Medical Student, Univ. of London). M.Sc. (Lond.) with mark of distinction. A.I.C. (1920). A.C.G.F.C. and Streathfield Memorial Prize, 1919. (*Signed by*) A. Prideaux Dawson, Arthur J. Hale, H. M. Atkinson.

HOYLE, JIM, 11, Crow Lane, Ramsbottom. British. Finisher (Woollen). 2nd and 3rd Year Certificates Chemistry gained at Blackburn Technical College. 1st, 2nd, 3rd, and 4th Year Chemical Trades Course. U.L.C.I., with distinction in Magnetism and Electricity. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

HUGHES, HORACE WILLIAM, 27, Ombersley Rd., Balsall Heath, Birmingham. British. Schoolmaster. B.Sc. (Birmingham), Class 1 (1921). Principal Subjects: Metallurgy, Chemistry; Subsidiary: Strength of Materials. (*Signed by*) Harold Harris, Thomas Turner, Wm. Wardlaw.

JACKSON, JOSEPH TAYLOR, B.Sc. (Lond.), 192, Algernon Road, Lewisham, S.E. 13. British. Lecturer in Applied Chemistry at The Leathersellers' Company's Technical College, S.E. 1. Bachelor of Science, London University. Fellow Royal Microscopical Society, London. War service (France and Salonika), Sept. 1914-Jan. 1919. (*Signed by*) Arthur Harden, Charles Dorée, S. Judd Lewis.

JERTU, DAVID BRET, 34, High Street, Welshpool, Montgomeryshire. British (Welsh). Research Student. B.Sc., University of Wales, First Class Honours. M.Sc., University of Wales. Associate of the Institute of Chemistry. Paper

Jehu and Hudleston, *Trans.*, 1924, 125, 1451. (*Signed by*) T. Campbell James, C. R. Bury, L. J. Hudleston, H. Medwyn Roberts.

JOBSON, WILLIAM, 52, The Mall, Swindon, Wilts. British. Analytical Chemist. Asst. Analyst in G. W. Rly. Chemical Laboratory, Swindon, for the last 25 years (less 4½ years' war service), appointed Chief Assistant, May 1922. Board of Education, S. and A. Dept., Inorganic Chemistry (Practical), Honours Part 1, 1903, Pass. (*Signed by*) W. R. Bird, T. C. Davison, T. Hartley.

JONES, CLIFFORD MERTON, Buxton Crescent, Newton Hill, Leeds Rd., Wakefield. British. University Student (post graduate). Science student at Queen Elizabeth's Grammar School, Wakefield (1914-1920). Laboratory assistant for two years (part time). Student in Science at University of Leeds, 1921 onwards. 2nd Class Honours B.Sc. in Chemistry, July 1924. (*Signed by*) J. B. Cohen, W. Lawson, W. A. Wightman.

JONES, THOMAS WILLIAM, 36, St. Vincent Road, Westcliff-on-Sea. English. Technical Chemist. B.Sc. (Hons. Chem.), London 1922. (*Signed by*) J. R. Partington, E. E. Turner, Stephen Miall, W. G. Shilling, F. A. Williams.

KEANE, JOHN, 6, Shamrock Villas, Drumcondra, Dublin. Irish. Assistant Lecturer in Chemistry, University College, Dublin. B.Sc. (First Hons.), 1917. M.Sc. 1918. Ph.D. 1922 (National University). (*Signed by*) A. G. G. Leonard, A. O'Farrelly, Sydney Young.

LUCY, ALFRED, 16, Chesney Street, Battersea, London, S.W. 11. British. Junior Assistant Chemist. Twelve years' Practical Chemical experience in Works and Research Laboratories (i.e., The Gas Lighting Improvement Co., Ltd.), etc. Chemistry student, attended classes up to and including the B.Sc. Standard in Theoretical and Practical Inorganic and Organic Chemistry. Battersea Polytechnic certificates for Inorganic Chemistry and Oils, Fats, and Waxes. (*Signed by*) William A. Godby, J. L. White, John Wilson.

MABBOTT, ERNEST EDWARD, 358, Fore Street, Edmonton, N. 9. British. Student. B.Sc. Engaged upon Organic Research work at East London College. (*Signed by*) J. R. Partington, E. E. Turner, A. T. Healey.

MCDOWALL, DAVID, 2, Kennishead Road, Thornliebank, Glasgow. British. Process Supervisor, Calico Printers, Ltd., 8 years, Manager, McDowall, Morrison & Co., Ltd., Chemical Manufacturers, and interested in research on behalf of Chemical Industry and in connection with Manufacturing Chemistry. (*Signed by*) Robert Craig McDowall, W. McHutchison, Andrew S. Matchett.

MANSKE, RICHARD H. F., The University, Manchester. British. Research Student in Chemistry, Victoria University, Manchester. B.Sc. 1923. M.Sc. 1924. Queen's University, Kingston, Canada. 1851 Exhibition Scholar, 1924—from Canada. (*Signed by*) Arthur Lapworth, R. Robinson, J. Kalf.

MOIR, HUGH CLOUSTON, 7, Craigielea St., Dennistoun, Glasgow. British. Chemist. Bachelor of Science (Applied Chemistry), Glasgow University. Associate of the Institute of Chemistry. Presently employed as Chemist by Wm. Beattie, Ltd., Dennistoun Bakery, 116, Paton St., Glasgow. (*Signed by*) G. G. Henderson, T. S. Patterson, S. Horwood Tucker.

MORTON, RICHARD ALAN, 2, Lumley Street, Garston, Liverpool. British. University Lecturer (Inorganic Chemistry). B.Sc., Ph.D. (Liv.), A.I.C. Several papers, *J.C.S.*, *Jour. Phys. Chem.* (*Signed by*) E. C. C. Baly, Harold Rogerson, I. M. Heilbron.

MOULDS, FREDERICK WILSON, Hill Crest, Villa Road, Nottingham. British. Chemist and Druggist. Member of the Pharmaceutical Society. Chemist

in charge of the Laboratories of Messrs. Newball & Mason, Ltd., Nottingham, and a director of the firm. Late student of the University College, Nottingham, where I studied Chemistry and Pharmacy, also Industrial Bacteriology. (*Signed by*) F. S. Kipping, J. B. Firth, F. C. Laxton, Wm. H. Sims.

MYLES, ANDREW JOSEPH, 12, Gardner Rd., Tue Brook, Liverpool. British. Works Manager and Chemist. 20 Years' experience in Tar Distillation and research work on Roads Compositions. Have written and read papers on treatment of and construction of modern road surfaces. Designed a viscometer for tar and bituminous compositions. (*Signed by*) George Tate, George S. Irvine, Thomas J. Roberts.

NASH, ALFRED WILLIAM, 18, Prospect Rd., Moseley, Birmingham. British. Professor of Oil Engineering and Refining. B.Sc. degree for original researches on the "Pyrogenesis of Hydrocarbons." "The Berginisation of Coal and Oil," author, *Journ. Inst. Pet. Technologists*, Vol. 10, 43. "Fuel Oil Resources of the Future," joint author, *Journ. Inst. Pet. Tech.*, Vol. 10, 47. "Somerset Oil-shales," joint author, *Journ. Inst. Pet. Tech.*, Vol. 10, 47. 1907-22, engaged in Oil Refineries—eventually General Manager. 1922-present, Birmingham University, Senior Lecturer, afterwards Professor. (*Signed by*) G. T. Morgan, A. E. Dunstan, Harold Harris.

OAKLEY, HENRY BOWEN, Wellcome Tropical Research Laboratories, Khartoum, Sudan. British. Assistant Government Research Chemist. Diploma of Imperial College. M.Sc. London. A.R.C.S. London. In conjunction with Prof. J. C. Philip, *J.C.S.*, 1924, 123, 1189. (*Signed by*) A. F. Joseph, James C. Philip, M. B. Donald.

PALMER, EDGAR KENT, Rose Bank, Victoria Rd., Hale, Altrincham. British. Post-graduate research. Oct. 1919-July 1923, Student at College of Technology, Manchester, in full-time degree course in the Chemical Technology of Textiles. July 1923, Grad. B.Sc.Tech. June 1924, Research under Prof. E. Knecht, Ph.D., and at present the same. (*Signed by*) Frank Lee Pyman, Edmund Knecht, John K. Wood.

POMERANTZ, DAVID, 15, Nottingham Place, Commercial Rd., E. 1. British. Student. Inter B.Sc. Two years at Royal College of Science for the 3 years necessary for the associateship (Chemistry). Am now doing the honours course at West Ham M. C. (*Signed by*) H. Bogdanor, George Dean, R. S. Glennie.

RAWLINGS, HARRY, 15, Station Road, Ramsey, Huntingdon. British. Science master (Chemistry). B.Sc. Lond., 2nd Hons. Chemistry, 1921. Assistant Analyst, Messrs. Boots Pure Drug Co., Ltd., 1915-17. Unpublished research on organic derivs. of tin, under Prof. Kipping at Univ. Coll., Nottingham, 1921 and early 1922. Chemistry student at Univ. Coll., Nottingham, 1917 and 1919-22. Am at present working for M.Sc. (Lond.) [May 1925], and desire access to the Library of the Society. (*Signed by*) F. S. Kipping, E. B. R. Prideaux, J. B. Firth.

REED, JOHN BRENT, 49, St. Mildred's Rd., London, S.E. 12. British. Assistant Research Chemist in the Research Laboratories of the South Metropolitan Gas Coy. Bachelor of Science, London. Associate of the Institute of Chemistry of Gt. Britain and Ireland. Student at Birkbeck College for the degree of Doctor of Philosophy. (*Signed by*) George Senter, S. Sugden, Walter T. J. Morgan, S. Medsforth.

RHODES, WILLIAM GEORGE, Park View, 318, Granville Rd. Park, Sheffield. English. Senior Science Master, Firth Park Secondary School, Sheffield. (*Signed by*) C. K. Ingold, John Evans, A. S. Russell.

ROBERTSON, GEORGE JAMES, M.A., B.Sc., Ph.D., The Manse, Strathkinness,

St. Andrews, Fife. British. Assistant in Chemistry and Carnegie Teaching Fellow in the University of St. Andrews. A thesis entitled "Investigations on Cellulose." Conjoint paper read by Principal Irvine before the American Chemical Society. (*Signed by*) J. C. Irvine, John Read, G. M'Owan.

SALMON, ROBERT JOSEPH, C.M.S. Medical Training College, Hangchow, Chekiang, China. British. Lecturer in Chemistry, Medical Training College, Hangchow. M.Sc. Manchester. (*Signed by*) Arthur Lapworth, Frederick Challenger, John F. Wilkinson, Harold Mastin, D. H. Bangham, Fred Fairbrother.

SHEPHERD, JOHN ROBERT, Lady Hall Farm, Broughton-in-Furness, Lancs. British. Chemist. M.Sc. (London) in Chemistry. A.I.C. (*Signed by*) Robert H. Pickard, J. Kenyon, J. L. White, A. Houssa, Harold Hunter.

SINGH, TERRAIN, alias PREM CHANDRA SHARMA, Engineering College Hostel, Benares Hindu University. Indian. M.Sc. Demonstrator in the Department of Industrial Chemistry of B.H.U. M.Sc. of the Benares Hindu University with a thesis on "The Effect of the Size of the Soil-particles and Electrolytes on the Equilibrium of Moisture between the Seed and the Soil." (*Signed by*) Phuldeo Sahay Varma, S. S. Bhatnagar, N. R. Dhar.

SMITH, ALAN LAWRENCE, Bank House, 22, Dean St., Blackpool. British. *Trans. Chem. Soc.*, 1923, 123, 1046-1055, "The Interaction of Hydrogen Sulphide, Thiocyanogen and Thiocyanic Acid on Unsaturated Compounds." M.Sc., Victoria University. (*Signed by*) Henry Stephens, Frederick Challenger, F. P. Burt, D. H. Bangham, Fred Fairbrother, John F. Wilkinson.

THORN, GEORGE, Grove House, Beechen Grove, Watford. British. Science Master, Boys' County School, Harrow. B.Sc. (Bristol). (*Signed by*) F. Francis, J. W. McBain, F. W. Rixon.

TOWNSEND, LEONARD WILLIAM ERNEST, 35, Harewood Rd., Collier's Wood, Merton, S.W. 19. British. Assistant Chemist at the South Metropolitan Gas Co., 709, Old Kent Rd., S.E. Student, five years' laboratory training. (*Signed by*) S. Medsforth, E. de Barry Barnett, P. C. L. Thorne.

WALKER, LESLIE JOHN, 45, Devereux Road, Wandsworth Common, S.W. 18. British. Student at the School of Pharmacy of the Pharmaceutical Society of Gt. Britain, 17, Bloomsbury Sq., W.C. 1. Pharmacist, have passed Qualifying Exam. of Pharmaceutical Society of Gt. Britain. Chemistry is included in this Exam., and it is my intention to continue studies in same. At present studying for Major Exam. of Pharmaceutical Society. (*Signed by*) C. E. Corfield, F. Browne, F. H. Lowe.

WALKER, THOMAS KENNEDY, 4, Swythamley Road, Cheadle Heath, Stockport. British. Research Chemist to the Institute of Brewing, Research Scheme Committee. Degrees: M.Sc., Ph.D., Victoria University of Manchester. Fellow of the Institute of Chemistry. Two years' research for the Admiralty, and for two years as Assistant Chemist to Sir R. Robertson, F.R.S., in the Research Department, Royal Arsenal, Woolwich. Three years' research in Organic Chemistry with Professor A. Lapworth, F.R.S., at Manchester University. For the past three years I have been assisting Professor F. L. Pyman, F.R.S., in investigations on the preservative principles of hops under the Institute of Brewing Research Scheme. Publications: "Preparation of Sodium Ethoxide from Caustic Soda" (*Journ. Soc. Chem. Ind.*, 1921, 40, 172r); "Condensation of Aryldiazonium Salts with Mono-alkylated Malonic Acids" (*J.*, 1923, 123, 2775); "Condensation of Aryldiazonium Salts and of Alkyl Nitrites with Cyanoacetic Acid Derivatives" (*J.*, 1924, 125, 1622); five other papers dealing with the antiseptics of hops, of which one was published jointly with Professor Pyman and Harold Roger.

son, Esq. (*Journ. Inst. Brew.*, 1922, 19, 929; 1923, 20, 373; 1924, 21, 570, 712). (*Signed by*) Frank Lee Pyman, Fredk. M. Rowe, Jas. Grant.

WATERS, WILLIAM ALEXANDER, 35, Shirley Road, Cardiff. British. Research Student in Chemistry (Resident B.A. of Gonville and Caius College, Cambridge). Cambridge Natural Sciences Tripos, Part I, Class I, Cambridge Natural Sciences Tripos, Part II (Chemistry), Class I. Shuttleworth Research Studentship in Chemistry at Caius College, Cambridge. (*Signed by*) Hamilton McCombie, Harold A. Scarborough, Eric K. Rideal.

WATSON, JAMES BERNARD, 30, Mulgrave Road, West Hartlepool. British. Metallurgical Chemist. Four years in the laboratory of the Technical College, West Hartlepool. Seven years as chemist in the Chemical and Metallurgical laboratory of the Central Marine Engine Works, West Hartlepool. (*Signed by*) J. W. Patterson, Gilbert Palmer, D. Arthur Ruell.

WATTS, ERNEST SWANN, "Eaglesfield," Limefield Road, Kersal, Manchester. British. Chief Chemist, E. Griffiths Hughes, Ltd., Manchester. Qualifying Examination of the Pharmaceutical Society of Great Britain. (*Signed by*) S. Ernest Melling, Harry Brindle, Chas. Turner.

WHAMOND, ARCHIBALD STEELE, 22, Church St., Alloa, Clackmannanshire. British. Analytical Chemist. Studied Chemistry at Heriot Watt College, Edinburgh, Day and Evening Classes, 1911-1914. March 1914-Nov. 1923, Assistant Chemist, Messrs. Wm. McEwan & Co., Ltd., Edinburgh (Army Service, Sept. 1914-Jan. 1919). Nov. 1923-present time, Chief Chemist, Messrs. Geo. Younger & Son, Ltd., Alloa. (*Signed by*) John M. Guthrie, A. Scott Dodd, John Doull.

WOODCOCK, EDWIN JOHN, "Stonecot," Claremont Hill, Jersey, C.I. British. Assistant Official Analyst. For the past 28 years Assistant to F. W. Toms, Esq., F.I.C., Official Analyst of Jersey, namely, the first five years as private assistant and since then as senior assistant analyst to the States of Jersey. (*Signed by*) F. W. Toms, Bernard Dyer, Alex. K. Miller, F. G. P. Remfry, G. Neville Huntly, R. Le Rossignol.

WORTHINGTON, JOHN STANLEY, 27, Rowena St., Great Lever, Bolton. British. Works Chemist. Experience in manufacture of Heavy Chemicals at Messrs. John Smith Junr. & Co., Ltd., Great Lever Chemical Works, Bolton, since 1908. Student in Advanced Chemical Tech. at Manchester College of Technology. At present have control of large Sulphuric Acid Plant. (*Signed by*) Arthur Worthington, Frank Lee Pyman, T. Trevor Potts.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2):

BELL, JAMES MUNSIE, Dept. of Chemistry, Univ. of North Carolina, Chapel Hill, N.C., U.S.A. Canadian. Professor of Chemistry. Head of Chemical Department, University of N. Carolina. Formerly in Bureau of Mines, Washington, D.C., U.S.A. Numerous original publications, chiefly in the *Journal of the American Chemical Society*. (*Signed by*) James W. McBain.

CAMERON, JOHN, Peking Union Medical College, Peking, Chihli, North China. British (Scotch). Pharmacist to the above-named institution. Member of the Pharmaceutical Society of Great Britain. Publications as per attached list to date (17 articles). Instructor in Pharmacy in British Army in France, 1917-18. Lecturer in Pharmacy and *Materia Medica* in Peking Union Medical College, 1920-25. (*Signed by*) A. E. Newland.

McINTYRE, GORDON, Sarnia, Ontario, Canada. Canadian. Chemist and Petroleum Technologist. Graduate McGill University, B.Sc., Ch.E. Chief

Chemist, Imperial Oil Refineries, Limited. (*Signed by*) Alfred Stansfield, Harold J. Roast.

THOMAS, Professor KARL, M.D., Leipzig, Liebig str. 16. German. Professor ordinar. für physiologische Chemie an der Universität, Leipzig, seit 1921. Mitarbeiter von Hoppe-Seylers Zeitschrift für physiologische Chemie (herausgegeben v. Kossel) und der Biochemischen Zeitschrift (herausgegeben von Neuberg). Schüler von W. Wislicenus, H. Thierfelder und Max Rubner, Mitglied der Biochemical Society. (*Signed by*) George Barger, Robert Robinson.

## ADDITIONS TO THE LIBRARY.

### I. Donations.

DUPARC, LOUIS, and BASADONNA, M. Manuel théorique et pratique d'analyse volumétrique. 2nd edition. By LOUIS DUPARC and PAUL WENGER. Paris 1925. pp. 214. ill. 18 fr. (*Recd.* 18/3/25.)

From the Publisher: M. Payot.

FRANZEN, HANS. Margarine. (Chem. Tech. in Einzeldarstellungen.) Leipzig 1925. pp. viii + 100. ill. Gm. 10. (*Recd.* 31/3/25.)

From the Publisher: Herr Otto Spamer.

INDUSTRIAL CHEMIST and chemical manufacturer: a journal devoted to the progress of applied chemistry and chemical engineering. Vol. I, etc. London 1925 +. (*Reference.*)

From the Publishers: The St. Margaret's Technical Press.

KÖNIGLICH PREUSSISCHEN AKADEMIE DER WISSENSCHAFTEN ZU BERLIN. Monatsberichte 1876 & 1881. Berlin 1877 & 1882. (*Reference.*)

From the Royal Society.

LUNGE, GEORGE. The manufacture of acids and alkalis. Completely revised and rewritten under the editorship of ALEXANDER CHARLES CUMMING. Vol. IV. The manufacture of sulphuric acid (contact process). By FRANK DOUGLAS MILES. London 1925. pp. xvi + 428. ill. 36s. net. (*Reference.*)

From the Publishers: Messrs. Gurney & Jackson.

ROYAL TECHNICAL COLLEGE, [GLASGOW]. Journal: being a record of some of the research work carried out in the College by the staff and senior students. No. 1. Glasgow 1924. pp. 138. ill. (*Reference.*)

From the Director.

THORPE, JOCELYN FIELD, and WHITELEY, MARTHA ANNIE. A student's manual of organic chemical analysis, qualitative and quantitative. London 1925. pp. x + 250. ill. 9s. net. (*Recd.* 19/3/25.)

From the Authors.

### II. By Purchase.

AMERICAN ENGINEERING COUNCIL. Industrial coal: purchase, delivery, and storage. New York 1924. pp. x + 420. ill. 21s. net. (*Recd.* 17/3/25.)

ANDRÉS, LOUIS EDGAR. Vegetable fats and oils: their practical



preparation, purification, properties, adulteration, and examination. 4th revised and enlarged English edition. By HERBERT BIRT-WHISTLE STOCKS. London 1925. pp. viii + 413. ill. 15s. net. (*Recd.* 17/3/25.)

BACK, E., and LANDÉ, A. Zeemaneffekt und Multiplettstruktur der Spektrallinien. (Struktur der Materie in Einzeldarstellungen.) Berlin 1925. pp. xii + 214. ill. M. 14.40. (*Recd.* 8/4/25.)

BASSETT, HENRY. The theory of quantitative analysis and its practical application. London 1925. pp. x + 308. 15s. net. (*Recd.* 25/3/25.)

BLAKE, ERNEST G. The seasoning and preservation of timber. London 1924. pp. xiv + 132. ill. 9s. 6d. net. (*Recd.* 17/3/25.)

BOHR, NIELS. The theory of spectra and atomic constitution. 2nd edition. Cambridge 1924. pp. x + 138. ill. 7s. 6d. net. (*Recd.* 25/3/25.)

BORN, MAX, assisted by FRIEDRICH HUND. Vorlesungen über Atommechanik. Vol. I. (Struktur der Materie in Einzeldarstellungen.) Berlin 1925. pp. x + 358. M. 15. (*Recd.* 8/4/25.)

COHEN, JULIUS BEREND. Practical organic chemistry. 3rd edition. London 1924. pp. xvi + 520. ill. 6s. 6d. net. (*Recd.* 25/3/25.)

FIELD, SAMUEL, and BONNEY, SAMUEL ROBERT. The chemical coloring of metals and allied processes. London 1925. pp. xx + 264. ill. 10s. 6d. net. (*Recd.* 25/3/25.)

FITGER, PETER. Racemisierungserscheinungen bei optisch-aktiven Sulfidsäuren. Lund 1924. pp. 134. M. 4. (*Recd.* 31/3/25.)

FOURNEAU, ERNEST. Organic medicaments and their preparation. Authorised translation by WILLIAM ARTHUR SILVESTER. London 1925. pp. x + 262. ill. 15s. net. (*Recd.* 17/3/25.)

GOOCH, FRANK AUSTIN, and BROWNING, PHILIP EMBURY. Outlines of qualitative chemical analysis. 5th edition. New York 1924. pp. viii + 184. ill. 7s. 6d. net. (*Recd.* 25/3/25.)

HODKIN, FREDERICK WILLIAM, and COUSEN, ARNOLD. A text-book of glass technology. London 1925. pp. xxiv + 552. ill. 42s. net. (*Recd.* 17/3/25.)

HOFMAN, HEINRICH OSCAR. Metallurgy of copper. 2nd edition. Revised by CARLE R. HAYWARD. New York 1924. pp. xiv + 420. ill. 25s. net. (*Recd.* 25/3/25.)

LAMBERT, THOMAS. Bone products and manures: a treatise on the manufacture of fat, glue, animal charcoal, size, gelatin, and manures. 3rd edition, revised and enlarged by HERBERT BIRT-WHISTLE STOCKS. London 1925. pp. viii + 284. ill. 10s. 6d. net. (*Recd.* 25/3/25.)

LOEB, JACQUES. Regeneration from a physico-chemical viewpoint. New York 1924. pp. xii + 144. ill. 10s. net. (*Recd* 17/3/25.)

LUCAS, ALFRED. Antiques : their restoration and preservation. London 1924. pp. viii + 136. 6s. net. (*Recd.* 25/3/25.)

NUGEY, A. L. Oil refinery specifications. Easton, Pa. 1924. pp. x + 210. ill. 25s. net. (*Recd.* 17/3/25.)

PARTINGTON, JAMES RIDDICK. A text-book of inorganic chemistry for university students. 2nd edition. London 1925. pp. xii + 1068. ill. 25s. net. (*Recd.* 25/3/25.)

PULSIFER, H. B. Structural metallography : an illustrated text with laboratory directions for students. Easton, Pa. 1924. pp. viii + 210. ill. 17s. 6d. net. (*Recd.* 17/3/25.)

RECTOR, THOMAS M. Scientific preservation of food. New York 1925. pp. xii + 214. 10s. net. (*Recd.* 17/3/25.)

REID, EBENEZER EMMET. Introduction to organic research. [New York 1924.] pp. viii + 344. 24s. net. (*Recd.* 6/4/25.)

RINNE, FRIEDRICH. Crystals and the fine-structure of matter. Translated by WALTER S. STILES. London 1924. pp. x + 196. ill. 10s. 6d. net. (*Recd.* 17/3/25.)

STILLMAN, JOHN MAXSON. The story of early chemistry. New York 1924. pp. xiv + 566. 18s. net. (*Recd.* 25/3/25.)

THRESH, JOHN CLOUGH, and BEALE, JOHN FOSTER. The examination of waters and water supplies. 3rd edition. London 1925. pp. xiv + 590. ill. 25s. net. (*Recd.* 17/3/25.)

### III. Pamphlets.

BOARD OF AGRICULTURE AND FISHERIES. Statutory rules and orders, 1908, No. 964. Adulterations. Fertilisers and feeding stuffs. The fertilisers and feeding stuffs (methods of analysis) regulations, 1908. London 1908. pp. 9.

GRÜN, RICHARD. Die Einwirkung des Sulfidgehaltes auf die Eigenschaften von Hochofenschlacken und Hüttenzementen. (From *Stahl und Eisen*, 1925, 45.)

HAROLD, CHARLES HENRY HASLER, and WARD, ARTHUR ROKEBY. Report on experimental work carried out at the Army School of Hygiene to demonstrate that chlorine gas in association with ammonia gas is a more efficient sterilizer of water than chlorine gas used alone or chloros or bleaching powder. (From the *J. Roy. Army Med. Corps*, 1924, 41.)

JOSEPH, ALFRED FRANCIS, MARTIN, FREDERICK JOHN, and HANCOCK, J. S. The electrical method for determining soil alkali. (From the *Cairo Sci. J.*, 1924, 12.)

# PROCEEDINGS

## OF THE

### CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, May 7th, 1925, at 8 p.m.,  
Professor J. C. PHILIP, O.B.E., D.Sc., F.R.S., Vice-President, in  
the Chair.

The CHAIRMAN referred to the loss sustained by the Society,  
through death, of the following Fellows :

	Elected.	Died.
Edward Wightman Bell .....	June 20th, 1889.	Jan. 29th.
Arthur Boake .....	Dec. 2nd, 1875.	April 12th.
William Dugdale Harland .....	Feb. 7th, 1878.	April 23rd.
Sir David L. Salomons .....	May 4th, 1876.	April 19th.
George Young .....	Dec. 4th, 1890.	April 3rd.

The CHAIRMAN announced :

1. That the following address of congratulation had been sealed  
and would be presented to the Royal University of Pavia on the  
occasion of the Centenary Celebrations of that University which  
were being held from May 20th to 22nd, 1925 :

*To the Rector, Senate, Professors, and Alumni  
of the Royal University of Pavia  
from The Chemical Society.*

The Chemical Society sends cordial greetings and felicitations  
to the illustrious University of Pavia on the completion of no less  
than eleven centuries of high service to mankind.

As representatives of a Science rooted in antiquity, we gratefully  
acknowledge the debt we owe to the members of your University  
who throughout the ages preserved ancient learning and extended  
the boundaries of knowledge, giving to us our heritage. We do  
not forget that the celebrated Lanfranc, one of your earliest and  
greatest teachers, carried the torch of learning to our country as  
Archbishop of Canterbury. Since her foundation the University  
of Pavia has given to the world many men distinguished for learning

and science—Alexander Volta, who pointed out new paths which now we follow, Camillus Golgi, the great neurologist, and many others whose genius we gratefully acknowledge.

We join with those who will be hastening from all parts of the world to lay before you their tribute of praise, and we hope that in the future renewed prosperity will be added to your illustrious past.

Signed on behalf of the Chemical Society.

ARTHUR W. CROSSLEY, *President*.

JOCELYN THORPE, *Treasurer*.

T. SLATER PRICE, } *Secretaries*.

C. S. GIBSON, }

F. G. DONNAN, *Foreign Secretary*.



Sealed this Seventh day of May, One Thousand Nine Hundred and Twenty Five.

2. That a copy of the works of the late Walthère Spring had been presented to the Library by the Belgian Chemical Society, and that this volume can be purchased from Monsieur J. Wauters, Secrétaire, Société Chimique de Belgique, 83, Rue Souveraine, Brussels, price 40 francs, post free.

The following were formally admitted Fellows of the Chemical Society: Alan D. Whitehead, Stuart R. Parsons, Leslie S. Theobald, J. F. J. Rule, and A. H. B. Bishop.

Certificates were read for the first time in favour of:

Maung Hla Baw, R-1, 64th Street, Danneedaw, Rangoon.

Joseph John Blackie, c/o Messrs. Duncan, Flockhart & Co., 104, Holyrood Road, Edinburgh.

Samuel Cyril Blacktin, M.Sc., 173, Ecclesall Road South, Sheffield.

Nirmal Boran Brohmachary, B.Sc., Ghugudanga-Post, 24, Porganas, Calcutta.

Gertrude Margaret Bullick, B.Sc., 43, Belsize Park, Hampstead, N.W. 3.

Ralph Edgar Cable, Queen's Gardens, Hong Kong.

Leslie Marshall Clark, B.A., Ph.D., A.I.C., 38, Park Road, Hampton Wick.

Clive Kear Colwell, B.A., Ormesty, Great North Road, N. 2.

Jan Coops, 25, Sireelinkplein, The Hague, Holland.

William George Corderoy, B.Sc., 35, Century Road, Walthamstow, E. 17.

Oswald Pilkington Cronshaw, 141, Blackburn Road, Great Harwood, Blackburn.

John Alexander Currie, B.A., B.Sc., 44, Phillimore Gardens, W. 8.

Thomas Dillon, University College, Galway.

Octave Charles Marie Dony, 30, Rue Émile Banning, Brussels.

William Edward Gibbs, D.Sc., 4, Stanley Villas, Runcorn.

Ernest Hartshorne, B.Sc.Tech., 12, Muriel Street, Broughton.

Arthur Harvey, 12, Chaldon Road, Fulham, S.W. 6.

Charles Richard Hennings, Ph.D., 19, St. Dunstan's Hill, E.C. 3.

Noel Waterman Vere Jones, Eastnook, Pakefield, Lowestoft.

Frank William Lynch, M.Sc., F.I.C., 89, Hazelbottom Road, Cheetham, Manchester.

Charles Lipshaw, 48, Lower Broughton Road, Salford.  
 James Arthur Prescott, The University, Adelaide.  
 Malik Karam Singh, B.Sc., Rawalpindi City, India.  
 Norman Heath Smith, B.Sc., Anglo-Persian Oil Co., Ltd., Abadan.  
 John Thurgood, B.Sc., Roseleigh, Elmwood Avenue, Harrow.  
 Shojiro Uchida, 12, Shinryudo-Machi, Azabu-Ku, Tokio.  
 John Henry Walker, A.I.C., Gourepore Works, Naihati, E.B.Ry., Bengal.

Messrs. H. Burton and J. N. Sugden were elected Scrutators, and a ballot for the election of Fellows was held, the following subsequently being declared elected as Fellows :

James Munsie Bell.	David Bret Jehu, M.Sc., A.I.C.
Niels Janniksen Bjerrum.	William Jobson.
Archibald Beresford Blunsden.	Clifford Merton Jones, B.Sc.
Geoffrey Alger Blyde.	Thomas William Jones, B.Sc.
Thomas Henry Bowles.	John Keane, M.Sc., Ph.D.
William Harrison Brindley, M.C., M.A., M.Sc.Tech., A.I.C.	Alfred Lucy.
James Lindsay Buchan, B.Sc.	Ernest Edward Mabbott, B.Sc.
Frank Henry Charles Bull, B.Sc., A.I.C.	David McDowall.
John Alfred Valentine Butler, M.Sc.	Gordon McIntyre, B.Sc., Ch.E.
Annie Lavinia Byford, B.Sc.	Richard H. F. Manske, M.Sc.
John Cameron.	Hugh Clouston Moir, B.Sc., A.I.C.
James Herbert Clegg.	Richard Alan Morton, B.Sc., Ph.D., A.I.C.
Horace Cecil Cockroft, B.Sc., A.I.C.	Frederick Wilson Moulds.
Francis Xavier Coyne.	Andrew Joseph Myles.
James Craik, M.A., B.Sc., Ph.D.	Alfred William Nash, B.Sc.
Herbert Greetham Dane, M.Sc.	Henry Bowen Oakley, M.Sc., A.R.C.S.
Harry Dean.	Edgar Kent Palmer, B.Sc.Tech.
Margaret Stedman Leonora Dixon.	David Pomerantz.
Robin George Westbury Farnell, A.R.C.S., A.I.C.	Harry Rawlings, B.Sc.
Irvine John Faulkner.	John Brent Reed, B.Sc., A.I.C.
Thomas Flett, B.Sc., A.I.C.	William George Rhodes.
Thomas James Elijah Gardner.	George James Robertson, M.A., B.Sc., Ph.D.
Richard Randolph Garrahan, B.Sc.	Robert Joseph Salmon, M.Sc.
John Charles Gilbin, B.Sc., A.I.C.	Prem Chandra Sharma, M.Sc.
Helen Simpson Gilchrist, B.Sc., Ph.D.	John Robert Shepherd, M.Sc., A.I.C.
Isabel Hodgson Hadfield, M.Sc.	Alan Lawrence Smith, M.Sc.
James Francis Halpin, F.I.C.	Karl Thomas, M.D.
Donald Hanson.	George Thorn, B.Sc.
Thomas Haworth.	Leonard William Ernest Townsend.
John Stanley Heaton, B.Sc., Ph.D.	Leslie John Walker.
John Cyril Hensman, M.A., A.I.C.	Thomas Kennedy Walker, M.Sc., Ph.D., F.I.C.
Joseph Hill.	William Alexander Waters, B.A.
Frederick Denison Maurice Hocking, M.Sc., A.I.C.	James Bernard Watson.
Jim Hoyle.	Ernest Swann Watts.
Horace William Hughes, B.Sc.	Archibald Steele Whamond.
Joseph Taylor Jackson, B.Sc.	Edwin John Woodcock.
	John Stanley Worthington.

The following papers were read :

- "The tautomerism of dyads. Part III. The effect of the triple linking on the reactivity of neighbouring atoms." By Mrs. E. H. INGOLD.
- "The rotatory dispersive power of organic compounds. Part XVI. Halogen-derivatives of camphor." By J. O. CUTTER, H. BURGESS, and T. M. LOWRY.
- "The isomerism of the oximes. Part XXII. The configuration of the aldoximes." By O. L. BRADY and G. BISHOP.
- "The parachor and chemical constitution. Part I. Polar and non-polar valencies in unsaturated compounds." By S. SUGDEN, J. B. READ, and H. WILKINS.
- "The tautomerism of dyads. Part IV. New evidence of the tautomeric mobility of oximes." By J. P. GRIFFITHS and C. K. INGOLD.

Ordinary Scientific Meeting, Thursday, May 21st, 1925, at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., Vice-President, in the Chair.

The CHAIRMAN referred to the loss sustained by the Society, through death, of the following :

	Elected.	Died.
Albin Haller (Honorary Fellow) .....	Feb. 6th, 1908.	May 1st.
Samuel Henry Davies .....	Feb. 15th, 1894.	May 9th.
John Mylne Mullaly .....	May 4th, 1922.	May 4th.

It was also announced that the Celebration of the Centenary of Faraday's discovery of benzene, which is being arranged by the Royal Institution in association with the Chemical Society, the Society of Chemical Industry, and the Association of British Chemical Manufacturers, will take place at the Royal Institution on Tuesday, June 16th, 1925. In the morning, at eleven o'clock, there will be a reception by the Duke of Northumberland of English and foreign delegates, and several short addresses will be delivered commemorative of Faraday's chemical work. In the evening, a banquet will be held in the Goldsmiths' Hall, the price of the tickets being £2 2s. each, including wine. Application for tickets for the reception and for the banquet, which are limited in number, should be made to the Secretary, The Royal Institution, Albemarle Street, W. 1.

Mr. H. G. Dane was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of :

Marion Alice Battie, B.Sc., A.I.C., The Orchard, Ivy Lane, Woking.  
 William Ambler Berry, B.Sc., 19, Blakeney Road, Sheffield.

Thomas Anthony Canning, Crindau Gas Works, Newport, Mon.  
 John Carroll Culbert, 172, North Road, Belfast.  
 Alexander John Dey, F.R.S.E., Rothiemay, Corstorphine, Edinburgh.  
 Stanley James Featherston, 33, Belmont Road, Beckenham.  
 James Hindle, 4, Plane Street, Blackburn.  
 Thomas Moore, B.Sc., 8, Cyprus Avenue, Belfast.  
 Alexander John Morrison, Testing Branch, Public Works Department,  
 Sydney, N.S.W.  
 Frank Richard Morrison, Brae Street, Waverley, Sydney, N.S.W.  
 Ernest Charles Padgham, 30, Churchill Road, N.W. 2.  
 John Monteath Robertson, B.Sc., A.I.C., The Chemistry Department, The  
 University, Glasgow.  
 Ernest Henry Warren, B.A., 1, Chamber's Lane, Willesden Green, N.W. 10.  
 James Watt, F.R.S.E., Craiglockhart House, Slateford, Edinburgh.  
 William John Willis, Hazel Mount, Carnforth.

The following Certificates have been authorised by the Council  
 for presentation to ballot under Bye-Law I (2) :

Howard Ecker, 1510, Dana Avenue, Cincinnati, Ohio, U.S.A.  
 William Beesley, Binnyston Gardens, Bangalore, India.  
 Alexander Smith, P.O. Box 103, Nairobi, Kenya Colony.

The following papers were read :

- "The rotatory dispersion of derivatives of tartaric acid. Part II.  
 Acetyl derivatives." By P. C. AUSTIN and J. R. PARK.
- "The stability of additive compounds between esters and acids."  
 By J. KENDALL and J. E. BOOGE.
- "Additive compounds in the ternary system, acid-ester-water."  
 By J. KENDALL and C. V. KING.
- "A spectroscopic study of the combustion of phosphorus trioxide  
 and of phosphine." By H. J. EMELÉUS.
- "The nature of the alternating effect in carbon chains. Part III.  
 A comparative study of the directive efficiencies of oxygen and  
 nitrogen atoms in aromatic substitution." By E. L. HOLMES  
 and C. K. INGOLD.

### LIST OF FELLOWS, 1925.

It has been decided to print the List of Fellows for 1925 and  
 to supply the List to those Fellows who make application to the  
 Assistant Secretary by the 31st July, 1925.

### BERICHTE, 1915 to 1924.

Sets of the Berichte from 1915 to 1924 (10 years) are now offered  
 to Fellows of the Society at £22, carriage extra. Application should  
 be made to Mr. S. E. Carr.

List of Papers, or Abstracts thereof, received between April 3rd and May 21st, 1925. (This List does not include the titles of papers which have been read at a Scientific Meeting, or which have appeared in the Journal.)

"The ionisation of aromatic nitro-compounds in liquid ammonia."

By M. J. FIELD, W. E. GARNER, and C. C. SMITH.

" $\alpha$ -Acenaphthoquinoline." By J. STEWART.

"Alcohols of the hydroaromatic and terpene series. Part IV.

$\alpha$ - and  $\beta$ -Fenchyl alcohols and some esters derived therefrom." By J. KENYON and H. E. M. PRISTON.

"Perkin's reaction." By T. HOPKINS.

"Action of zinc alkyl halides on nitric esters." By T. HOPKINS.

"Polynuclear heterocyclic aromatic types. Part II. Some anhydronium bases." By J. W. ARMIT and R. ROBINSON.

" $\beta$ -Piperonylpropionitrile and some derived substances." By W. BAKER and R. ROBINSON.

"The melting points of benzene derivatives." By T. BEACALL.

"Nitrosation of phenols. Part II. 3-Bromo-, 2-bromo-, 3-iodo-, and 2-iodo-phenols, with evidence favouring the nitroso form for 4-nitroso phenol." By H. H. HODGSON and F. H. MOORE.

"The Kekulé formula for benzene and the existence of isomeric ortho disubstitution products." By H. H. HODGSON and J. H. WILSON.

"A new method of diagnosing potential optical activity. Part I. The optical activity of chlorobromomethanesulphonic acid." By J. READ and A. M. McMATH.

"The carboxy-phenyl camphoramic acids." By M. SINGH and R. SINGH.

"A simplified method of micro-combustion: the micro-Dennstedt method." By C. FUNK and S. KON.

"Interfacial tension." By J. R. POUND.

"Low temperature oxidation at charcoal surfaces. Part I. The behaviour of charcoal in the absence of promoters." By E. K. RIDEAL and W. M. WRIGHT.

"Osmotic pressure by the solubility method in concentrated solutions." By M. P. APPLEBEY and P. G. DAVIES.

"Synthetical experiments in the naphthyridine groups." By J. M. GULLAND and R. ROBINSON.

"Chlorobenzothiazole dibromide." By R. F. HUNTER.

"Note on the action of sodium of chlorobenzothiazole." By R. F. HUNTER.

"Investigations into the analytical chemistry of tantalum, niobium, and their mineral associates. Part III. A new method for



- the separation of tantalum from niobium. Part IV. The detection and determination of tantalum in niobium compounds." By A. R. POWELL and W. R. SCHOELLER.
- "The conditions underlying the formation of unsaturated and cyclic compounds from halogenated open-chain derivatives. Part VII. The influence of the phenyl group on the formation of the *cyclopropene* ring." By W. HAERDI and J. F. THORPE.
- "Rapid determination of copper and iron in mixtures of their salts." By A. S. RUSSELL.
- "The bromination of 4'-amino-1-phenyl-5-methyl benzothiazole and of 1:1-bisbenzothiazole." By R. F. HUNTER.
- "Amino benzothiazoles. Part I. 1-Phenylamino benzothiazole and its homologues." By R. F. HUNTER.
- "The directing influence of the methane sulphonyl group." By R. F. TWIST and S. SMILES.
- "The dissociation constants of selenious acid." By J. S. WILLCOX and E. B. R. PRIDEAUX.
- "The velocity of benzylation of certain amines. Part II." By D. H. PEACOCK.
- "Measurements of energy absorption of certain photo-chemical reactions with iodine." By B. K. MUKERJI and N. DHAR.
- "The action of hydrogen peroxide on limonene." By J. SWORD.
- "Synthetical experiments in the *isoquinoline* group. Part I." By R. D. HAWORTH and W. H. PERKIN.
- "Synthetical experiments in the *isoquinoline* group. Part II." By R. D. HAWORTH, W. H. PERKIN, and J. RANKIN.
- "Synthetical experiments in the *isoquinoline* group. Part III." By R. D. HAWORTH and W. H. PERKIN.
- "Synthetical experiments in the *isoquinoline* group. Part IV." By R. D. HAWORTH and W. H. PERKIN.
- "Synthesis of  $\psi$ -protoberberine and  $\psi$ -protopapaverine." By J. S. BUCK, W. H. PERKIN, and T. S. STEVENS.
- "Note on a laboratory method of preparing *p*-benzoquinone." By R. CRAVEN and W. A. T. DUNCAN.
- "Hydroxybenzils." By J. T. MARSH and H. STEPHEN.
- "Researches on sulphuryl chloride. Part III. Influence of catalysts on the chlorination of toluene." By O. SILBERRAD, C. A. SILBERRAD, and B. PARKE.
- "The adsorption of water from the gas phase on plane surfaces of glass and platinum." By I. R. MCHAFFIE and S. LENHER.
- "The action of phosphorus pentachloride on 2-isonitroso-1-hydrindones." By R. D. HAWORTH and H. S. PINK.
- "Oxidation products of oleic acid. Part I. Conversion of oleic acid into dihydroxystearic acid and the determination of the

- higher saturated acids in mixed acids from natural sources." By A. LAPWORTH and E. N. MOTTRAM.
- "The spatial structure of *cycloparaffins*. Part I. A new aspect of Mohr's theory and the isomerism of decahydronaphthalene." By W. A. WIGHTMAN.
- "The absorption spectra of the vapours of anthracene and anthraquinone, phenanthrene, and phenanthraquinone, and other quinones." By J. E. PURVIS.
- "Investigations on the dependence of rotatory power on chemical constitution. Part XXVII. Some esters of *p*-toluene-sulphonic and -sulphinic acids." By H. PHILLIPS.
- "Oxidations in turpentine and olive oil." By E. WALKER.
- "Colour and molecular geometry. Part IV. Explanation of the colours of the cyanine dyes." By J. MOIR.
- "The surface tensions of aqueous phenol solutions. Part II. Activity and surface tension." By A. K. GOARD and E. K. RIDEAL.
- "Triad groups in complexes of octahedral symmetry." By J. D. M. SMITH.
- "Isoquinoline derivatives. Part IX. Preparation and reduction of isoquinoline and its derivatives." By R. FORSYTH, C. I. KELLY, and F. L. PYMAN.
- "The nitration of *m*-meconine." By J. N. RÂY and R. ROBINSON.
- "Chenopodium oil. Part II. The hydrocarbon fraction." By T. A. HENRY and H. PAGET.
- "The amino- $\gamma$ -pyridones." By W. H. CROWE.
- "Studies of the glucosides. Part III. The synthesis of thioindican." By J. CRAIK and A. K. MACBETH.
- "The reduction of the bromoanthraquinones." By E. DE B. BARNETT and J. W. COOK.
- "The chlorination of acetanilide and the chloroamine-chloroanilide transformation." By F. G. SOPER.
- "The thermal decomposition of ozone." By R. O. GRIFFITH and A. McKEOWN.
- "Studies of electrolytic polarisation. Part III. The diffusion layer." By S. GLASSTONE.
- "Theories of polar and non-polar free affinities. A practical and theoretical reply to some recent criticisms and comparisons." By G. N. BURKHARDT and A. LAPWORTH.
- "The reaction between sodium hypobromite and urea." By M. B. DONALD.
- "Echitamine." By J. A. GOODSON and T. A. HENRY.
- "The preparation of phthalamic acids and their conversion into anthrenilic acids." By E. CHAPMAN and H. STEPHEN.

- "An X-ray examination of maleic and fumaric acid." By K. YARDLEY.
- "The estimation of arsenic in organic compounds." By G. NEWBERRY.
- "The bromination of acyl derivatives of phenylhydrazine: the preparation of 2:4-dibromophenylhydrazine." By J. E. HUMPHRIES and R. EVANS.
- "The system chromium trioxide-boric acid-water." By L. F. GILBERT.

CERTIFICATES OF CANDIDATES FOR ELECTION AT  
THE BALLOT TO BE HELD AT THE ORDINARY  
SCIENTIFIC MEETING ON THURSDAY, JUNE 18TH,  
1925.

BATTIE, MARION ALICE, The Orchard, Ivy Lane, Woking, Surrey. British. Post-graduate student. B.Sc. Honours (Chemistry), Class II. Associate of the Institute of Chemistry. (*Signed by*) T. S. Moore, Mary Boyle, S. Smiles.

BAW, MAUNG HLA, R-1, 64th Street, Danneadaw, Rangoon. Burmese. Analytical Chemist, Messrs. E. M. D'Souza & Co., Rangoon, and Science Master, St. John's College, Rangoon. Passed the Intermediate Examination in Science of the Calcutta University in 1916, taking Chemistry, Physics, and Mathematics. Process Chemist (1916 to 1921) at the Seikkyi Refinery of Messrs. The Indo Burma Petroleum Co., Ltd.; and Process Chemist (1922) in the acid works of The Burma Chemical Industries, Ltd. Process Chemist (1923) with The Rangoon Pharmaceutical and Chemical Works, Rangoon. Since 1924 chemist in charge of the analytical laboratory of Messrs. E. M. D'Souza & Co., Rangoon, and Science Master, St. John's College, Rangoon. (*Signed by*) Maung Tun Tin, Maung Ba, Maung Ba San.

BERRY, WILLIAM AMBLER, 19, Blakeney Rd., Sheffield. British. Research Student at University of Sheffield. B.Sc., Hons. Chem., 1924. Joint author with Dr. G. M. Bennett of the Note, *J.C.S.*, 1925, 127, 910. (*Signed by*) W. P. Wynne, T. M. Lowry, G. M. Bennett, F. G. Tryhorn.

BLACKIE, JOSEPH JOHN, c/o Duncan, Flockhart & Co., 104, Holyrood Road, Edinburgh. British. Pharmaceutical Chemist. Minor and Major Examination, Pharmaceutical Society of Great Britain. Laboratory Manager of Messrs. Duncan, Flockhart & Co., Manufacturing Chemists, Edinburgh. Examiner in Chemistry of the Pharmaceutical Society of Great Britain. (*Signed by*) George Barger, William Duncan, Eric Knott.

BLACKTIN, SAMUEL CYRIL, 173, Ecclesall Road South, Sheffield. British. Research Assistant. (Junior Assistant, Safety in Mines Research Laboratories, Badger Lane, Sheffield.) M.Sc. (Sheffield). (*Signed by*) W. P. Wynne, F. G. Tryhorn, J. Kenner.

BLIGH, NEVILLE MELTON, 67, Castle Road, Bedford. British. Science Master. A.R.C.S. (Chemistry), London, 1921. A.I.C., 1923. Formerly Senior Science Master, Wimborne Grammar School, Dorset. At present (Temporary) Senior Science Master, Stevenage Grammar School, Herts. (*Signed by*) H. B. Baker, James C. Philip, M. A. Whiteley.

BORLAND, HUGH ALEXANDER MILLAR, 14, Cotham Road, Bristol. British.

Teacher of Chemistry. A.R.C.S. (Lond.). M.Sc. (Bristol). Lecturer on Chemistry 1896 to present date (Secondary and Technical). Lecturer on Applied Chem., University of Bristol, 1910-19. (*Signed by*) Arthur Marsden, F. Francis, J. W. McBain, F. W. Rixon.

BROHMACHARY, NIRMAL BORAN, Ghugudanga-Post 24 Porganas, Calcutta, India. Hindu (Indian). Chemist to Messrs. B. K. Paul's Chemical and Pharmaceutical Works, Dum Dum, Calcutta. Passed the B.Sc. examination of the Calcutta University in 1920. Worked as an analytical and manufacturing chemist. Assistant of Messrs. Smith, Stanistreet & Co. for 2 years, and at present working as the Chemist for Messrs. B. K. Paul & Co. (for last three years). (*Signed by*) Dharendra Nath Mukerji, Sudhindranarayan Ray, R. L. Jenks.

BULLICK, GERTRUDE MARGARET, 43, Belsize Park, Hampstead, N.W. 3. British. Hons. Student in Chemistry, Bedford College, Univ. of London. Graduate of Lond. Univ. B.Sc., June, 1924. (*Signed by*) Holland Crompton, J. F. Spencer, M. S. Crewdson, J. Stewart.

CABLE, RALPH EDGAR, Queen's Gardens, Hong Kong. English. Apothecary, Medical Department, Hong Kong. Lecturer (part time), University of Hong Kong, Med. Faculty, Practical Pharmacy. (*Signed by*) R. W. E. Stickings, A. J. Ewins, G. Newbery, P. Blenkinsop.

CANNING, THOMAS ANTHONY, Crindau Gas Works, Newport, Mon. English. Gas and Chemical Engineer, now General Assistant Technical Engineer to the Newport (Mon.) Gas Company. Certificates in Chemistry granted by Institution of Gas Engineers. Engaged 7 years in Gas Manufacture and allied work and the chemistry of same. I desire to become a Fellow of the Chemical Society in order to keep in touch with current chemical literature. (*Signed by*) Geo. R. Thompson, H. E. Cox, J. H. Canning.

CLARK, LESLIE MARSHALL, 38, Park Rd., Hampton Wick, Kingston-on-Thames. English. Chemist, National Physical Laboratory, Teddington. Late Scholar and Research Scholar, Sidney Sussex College, Cambridge. Late Assistant Demonstrator, Cambridge University Chemical Laboratory. B.A., Cantab. Ph.D., London. Associate of Institute of Chemistry. Joint author of papers in *J.C.S.*, 1923, 123, 2353, and 2362. (*Signed by*) M. Johnson, Guy Barr, Percy G. Ward.

COLWELL, CLIVE KEAR, Ormesty, Great North Road, N. 2. English. Analytical and Consulting Chemist. B.A., Cantab. Paper in conjunction with A. J. Berry, M.A., in Chemical News. (*Signed by*) A. H. M. Muter, Cyril Dickinson, J. Kear Colwell.

COOPS, JAN, den Haag, 25 Sireelincplein. Dutchman. Dr. ir. Delft, Assistant, Commercial University, Rotterdam. Author of some papers in *Rec. trav. chim.*, 1920, 1921, 1922, 1923, 1924, 1925, *Chem. Weekblad*, and *Kon. Akad. van Wet. Amsterdam*, etc. (*Signed by*) H. J. Backer, Ernest Cohen, A. Smits.

CORDEROY, WILLIAM GEORGE, 35, Century Rd., Walthamstow, E. 17. British. Student for Teaching Profession (entering profession next Sept.). 1st Honours (Chem.), B.Sc. (Lond.). [Studied at East London College, 1921-24.] (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones, Elwyn Roberts.

CRONSHAW, OSWALD PILKINGTON, 141, Blackburn Road, Great Harwood, near Blackburn. British. Chemist and Assistant Gas Engineer, Accrington District Gas and Water Board. For past 3 years Chief Chemist to the Accrington District Gas and Water Board, having full chemical control of all gas manufacturing operations, the manufacture of sulphate of ammonia,

etc. Hold 1st Class Certificates Gas Manufacture (City and Guilds). Distinction in Inorganic Chemistry (Lanc. and Cheshire Inst.). 1st Class Certificate Inorganic and Organic Chemistry at Blackburn College of Technology. Associate Member of Institution of Gas Engineers. (*Signed by*) James Booth, John S. Morrison, Robert C. McDowall.

CULBERT, JOHN CARROLL, 172, North Road, Belfast. British. Pharmacist. Pharmaceutical Chemist, Member of Pharm. Society of Ireland, ex-Member Council of Pharm. Society of Ireland. (*Signed by*) George Scott Robertson, W. H. Gibson, Henry Wren.

CURRIE, JOHN ALEXANDER, 44, Phillimore Gardens, London, W. 8. British. Student. Honours B.A., Chemistry, and B.Sc., Oxford. Now researching under Professor Donnan at University College, London. (*Signed by*) F. G. Donnan, W. E. Garner, C. W. Bonnicksen.

DEX, ALEXANDER JOHN, Rothiemay, Corstorphine, Edinburgh. British. Manufacturing Chemist. Managing Director, T. and H. Smith, Ltd., Manufacturing Chemists. F.R.S.E. (*Signed by*) James Walker, Alex. C. Cumming, Alexander Lauder.

DILLON, THOMAS, University College, Galway. Irish. Professor of Chemistry, University College, Galway. Papers on Waxes, *Proc. R.D.S.*, 1909, vol. 12, No. 20; vol. 15, No. 10; *Proc. R.I.A.*, vol. 29, sec. B, No. 8. On separation of Isotopes of Lead, *Proc. R.D.S.*, 1922, vol. 17, p. 53. (*Signed by*) A. G. G. Leonard, Sydney Young, Emil A. Werner, A. O'Farrelly.

DONY, OCTAVE CHARLES MARIE, Bruxelles, 30 Rue Emile Banning. Belge. Professeur à l'Université de Bruxelles (Faculté de Science appliquées). Membre de l'Académie royale de Belgique. (*Signed by*) C. S. Gibson, Eric K. Rideal, T. M. Lowry, W. J. Pope, Henry E. Armstrong.

FEATHERSTON, STANLEY JAMES, 33, Belmont Rd., Beckenham, Kent. British. Analytical Chemist in Laboratory of Manufacturing Chemists, namely, Messrs. Hopkins & Williams, 16-17, Cross St., E.C. Honours Student in Chem. at Birkbeck Coll., University of London. 5 Years analytical work with manufacturing chemists. (*Signed by*) George Senter, F. Barrow, Samuel Sugden.

GASKILL, MALCOLM SINCLAIR, 3, Buckingham Rd., Hilton Park, Prestwich, Manchester. British. Chemical Engineer, West's Gas Improvement Co., Ltd., Manchester. Associate of the Manchester College of Technology. Chemist and Assistant Manager, Messrs. Hardman & Holden, Ltd., Chemical Manufacturers, Clayton. Present position, as above. Desirous of keeping in touch with modern developments of pure and applied chemistry. (*Signed by*) Harold G. Colman, William Buckley, Joseph Poulson.

GIBBS, WILLIAM EDWARD, 4, Stanley Villas, Runcorn. British. Chief Chemist to the Salt Union, Ltd. D.Sc. (Liverpool). Author of books: "Clouds and Smokes: The Properties of Disperse Systems in Gases," "The Dust Hazard in Industry." *Journ. Inst. Metals*, XV (1916), 1, pp. 41-191; *J.S.C.I.*, XLI, pp. 189-196; *Faraday Soc.*, XI, 1915, pp. 295-297, etc. (*Signed by*) W. C. McC. Lewis, I. M. Heilbron, E. C. C. Baly.

HAMER, NORMAN, "Ash Mount," Holcombe, nr. Manchester. British. Research and Analytical Chemist in Calico Printing, Dyeing, and Bleaching Works. As a student I have gained the Associateship of the Manchester College of Technology (Assoc. M.C.T.), whilst my duties as chemist cover a fairly wide field of analytical work, together with the investigation of the many and varied problems which are continually arising in the works. (*Signed by*) Arthur M. Morley, John K. Wood, Frank Lee Pyman.

HARTSHORNE, ERNEST, 12, Muriel St., Broughton, Manchester. British.

Chemist in the Laboratory of Dr. A. K. Miller, F.C.S. Degree of Bachelor of Technical Science in General Chemical Technology, Victoria University, Manchester. (*Signed by*) Alex. K. Miller, Frank Lee Pyman, John K. Wood.

HARVEY, ARTHUR, 12, Chaldon Road, Fulham, S.W. 6. British. Chemist. Formerly Agricultural Analyst, South Eastern Agricultural College (Univ. Lond.), Wye, Kent. Formerly lecturer on Applied Chemistry, Leather-sellers College, London. Author of "Practical Leather Chemistry" and "Tanning Material," published by Crosby Lockwood & Son. Also several papers on leather chemistry in *J. Soc. L. Trades Chem.* Editor of Abstracts, *J. Soc. L. Trades Chem.* Member, British Association of Chemists, American Chemical Society, Society of Leather Trades Chemists. (*Signed by*) M. C. Lamb, A. B. Bradley, R. W. West.

HENNING, CHARLES RICHARD, 19, St. Dunstan's Hill, London, E.C. 3. German. Consulting Chemist. Qualified Pharmaceutical Chemist. Graduated in Chemistry. Ph.D., Freiburg. Papers as given before when first being admitted. (*Signed by*) Otto Oberländer, George P. Forrester, A. W. Edwards.

HINDLE, JAMES, 4, Plane St., Blackburn, Lancs. British. Student. Have been full-time day student in the Chemistry Dept. Municipal Technical College, Blackburn, for four years and am now preparing for Hons. Chemistry, B.Sc. (Lond.) there. (*Signed by*) G. W. F. Holroyd, Harry G. Leigh, J. T. Holden.

JONES, NOEL WATERMAN VERE, Eastnook, Pakefield, Lowestoft. British. Student. Have been studying Chemistry for five years and wish to keep abreast of modern advances. (*Signed by*) E. de Barry Barnett, James W. Cook, Marcus A. Matthews.

LINCH, FRANK WILLIAM, 89, Hazelbottom Rd., Cheetham, Manchester. British. Research Chemist, British Dyestuffs Corporation. M.Sc., Lond. 1st Hons. Chemistry at B.Sc. F.I.C. Asst. Chief Chemist, H.M. Factory, Queensferry, 1915-1917. Chief Chemist, H.M. Factory, Avonmouth, 1917-1919. 1919 to date, Research Chemist, British Dyestuffs Corp., Blackley, Manchester. Action of sodium hypobromite on carbamide derivs. Part I. 3-Amino-coumarin. Both papers in *Trans.* 1912. (*Signed by*) G. R. Clemo, Colin H. Lumsden, Anthony J. Hailwood.

LIPSHAW, CHARLES, 48, Lr. Broughton Rd., Salford. British. Chemist to Messrs. Halliday & Co., Ltd., Bankfield Mills, Stockport. 4 years Laboratory Chemist, and Assistant Works Chemist, at Lowerhouse Printworks, Burnley. Student at the Royal Technical College, Salford. Diploma of the College, City and Guilds of London Institute, Final Certificates in Dyeing and Textile Printing. (*Signed by*) S. N. Brown, V. Edge, E. Clark, B. Prentice.

MOORE, THOMAS, 8, Cyprus Avenue, Belfast. British. Student. Graduate of London (with Honours) and of the Queen's University, Belfast. Fifth year research student in Photochemistry. (*Signed by*) Wm. H. McVicker, Joseph K. Marsh, A. W. Stewart, H. Graham.

NIXON, IVOR GRAY, 75, The Vale, Golder's Green, N.W. 11. English. Student. Have studied chemistry for over 6 years and desire to keep abreast of modern developments. (*Signed by*) E. de Barry Barnett, P. C. L. Thorne, James W. Cook.

OCULESHAW, VINCENT JOSEPH, 22, Bryn Street, Ashton-in-Makerfield, nr. Wigan. British. Lecturer and Demonstrator in Inorganic Chemistry. M.Sc. (Liv.). A.I.C. (*Signed by*) E. C. C. Baly, J. T. Nance, A. O. Jones.

PADGHAM, ERNEST CHARLES, 30, Churchill Road, N.W. 2. British. Research Assistant at the British Museum Laboratory. Trained in Analytical

Chemistry under the late Dr. Ludwig Mond, F.R.S., and the late Dr. B. Mohr, 1891-1896. Assistant at the Davy Faraday Research Laboratory of the Royal Institution, 1896-1918. Research Assistant at The British Museum Laboratory since 1920. (*Signed by*) Alexander Scott, H. J. Plenderleith, John W. Heath.

PRESCOTT, JAMES ARTHUR, The University, Adelaide, South Australia. British (England). Professor of Agricultural Chemistry at the Waite Agricultural Research Institute of the University of Adelaide. Papers on Soil Chemistry in the "Journal of Agricultural Science," VI, 111; VIII, 65, 111, 136; IX, 216; X, 177; XIII, 333; also Bulletins of the Sultanic Agricultural Society, Egypt. Research Scholar, Rothamsted Experimental Station, 1912-1916. Chief Chemist, Sultanic Agric. Soc., Egypt, 1916-1924. Proceedings, vol. 30, No. 123, 1914. (*Signed by*) Edward H. Rennie, E. J. Russell, H. B. Dixon, Arthur Lapworth, Robert Robinson, H. J. Page.

ROBERTSON, JOHN MONTEATH, Nether Fordun, Auchterarder, Perthshire. Scottish. Research Assistant. B.Sc. (Hons. Chem.), Glasgow, 1923. A.I.C., 1924. Strang-Steel Research Scholar, 1923-24. Carnegie Research Scholar, 1924-25. (*Signed by*) S. Horwood Tucker, T. S. Patterson, G. G. Henderson, R. Wright, David T. Gibson.

RUBENSTEIN, LEON, Jesus College, Oxford (Rookwood, 87, Eaton Grove, Swansea). British. Research Student for Doctorate of Philosophy (Oxford University). First Class Honours, Degree of Bachelor of Science (Welsh Univ.). Bachelor of Science (Oxford Univ.). "Substitution in Vicinal Trisubstituted Benzene Derivatives" (November 1923). (*Signed by*) W. H. Perkin, S. G. P. Plant, J. F. S. Stone, R. H. Griffith, R. D. Haworth.

SINGH, MALIK KARAM, Rawalpindi City. Indian (British subject). Paper Expert. I am a B.Sc. (Physics and Chemistry). Was granted a "State Technical Scholarship" by the Govt. of India for the study of the Paper-making industry in Gt. Britain and other Western countries. Before going to England I worked for about twenty months in the Bengal Paper Mills, Raneegunj (near Calcutta), during 1918-20. Joined College of Technology, Manchester, in 1920. During 1920-21 I completed in one year, a two years' course in paper making, and in the final examination I got a 1st class both in the theoretical and practical parts of the subject. I also studied the following subjects: Organic Chemistry, Physical Chemistry, Chemistry of Dyeing, Chemistry of the Colouring Matters, Economics, Chemical Engineering, Heat Engines, and Construction of Works. In 1921-22 (about 15 months) I received practical training in the following three paper mills, in Aberdeen, Scotland, making different classes of paper: (1) The Donside Paper Mills; (2) The Alex Pirie Paper Mills at Stonewood, and (3) The Mugiemooss Paper Mills at Bucksburn. During 1922-24 I conducted a special research on about a score of Indian raw materials, with a view to ascertain their suitability for making paper. I have paid short visits lasting from one to ten days to about a score of other paper mills and paper mill machinery manufacture workshops. I have seen almost all the paper mills in India. (*Signed by*) John K. Wood, Frank Lee Pyman, F. M. Rowe.

SMITH, NORMAN HEATH, Hillcroft, Spencer Avenue, Leek, Staffs. British. Process Chemist, at present with Messrs. Anglo-Persian Oil Co., Ltd., Abadan, Persia. B.Sc. (Tech.). Post grad. research on vegetable oils; 2½ years with Messrs. The British Aluminium Co., Ltd., as Asst. Chemist, and over 2 years with Messrs. Anglo-Persian Oil Co., Ltd. (*Signed by*) Colin E. Spearing, S. W. Hayter, H. Harper.

**STREATHER, ALEC THOMAS**, 3, Wellington Road, Watford. British. Works Chemist. B.Sc. (Honours Chemistry), Birmingham, 1922. Associate Institute of Chemistry. (*Signed by*) G. T. Morgan, S. R. Carter, C. E. Wood, F. W. Pinkard.

**THURGOOD, JOHN**, "Roseleigh," Elmwood Ave., Harrow, Middx. British. Analytical and Research Chemist. Engaged for 4 years in laboratory of Dunlop Rubber Co., Birmingham. Graduated B.Sc. at Birmingham University in 1922. At present engaged as Assistant Chemist to British Oxygen Co., Ltd., N. Wembley. (*Signed by*) G. T. Morgan, C. E. Wood, E. Holmes.

**TREW, VIOLET CORONA GWYNNE**, 18, Adam Street, Portman Square, W. 1. British. Student at Bedford College (London University). Reading for an Honours Degree in Chemistry. (*Signed by*) J. F. Spencer, H. Crompton, P. V. McKie.

**UCHIDA, SHOJIRO**, 12, Shinryudo-Machi, Azabu-Ku, Tokio, Japan. Japanese. Research Chemist of the Fuel Research Board of Japan. Undergraduate of Department of Chemistry, College of Technology, University of Tokio, Japan. (*Signed by*) W. A. Batley, V. H. Legg, M. J. Burgess, F. V. Tideswell.

**WALKER, JOHN HENRY**, A.R.T.C., A.I.C., Gourepore Works, Naihati, E.B. Ry., Bengal, India. Scotch. Chemist and Oil-mill Manager. Student Royal Technical College, Glasgow. Student with late Dr. J. Lewkowitsch. Sundry papers in *Analyst* and in *J.S.C.I.* Chemist and latterly mill-manager, Gourepore Co., Ltd., Linseed Oil. (*Signed by*) G. G. Henderson, Thomas Gray, F. J. Wilson.

**WARREN, ERNEST HENRY**, 1, Chamber's Lane, Willesden Green, N.W. 10. English. Research Student. B.A., Cantab. (*Signed by*) Robert Robertson, Geo. Stubbs, P. J. Sageman.

**WATT, JAMES**, Craiglockhart House, Slateford, Edinburgh. British. Writer to the Signet. Chairman of Directors, T. and H. Smith, Ltd., Chemical Manufacturers. F.R.S.E. (*Signed by*) James Walker, Alex. C. Cumming, Alexander Lauder.

**WILLIS, WILLIAM JOHN**, Hazel Mount, Carnforth, Lancs. English. Chief Valuer to Michael Faraday and Partners, 77, Chancery Lane, W.C. 2. 3 years' Assistant Demonstrator, Inorganic Chemistry, Barrow Technical School. 3 years' Lecturer on Metallurgy and Iron Foundry Practice, Bradford Technical College. 1st Class Honours Inorganic Chemistry, Science and Art Department. 1st Class Honours and Bronze Medal, City and Guilds of London, Iron and Steel Manufacture. 1st Class and Silver Medal, City and Guilds of London, Salt Manufacture. 8 years Analytical Chemist, Barrow Hematite Steel Co., Ltd. 6 years Chief Chemist and Assistant Works Manager, Yorkshire Iron and Coal Co., Ltd. 5 years Chief Valuer to Michael Faraday and Partners, Surveyors and Valuers. (*Signed by*) T. A. Henry, A. E. Bond, Harry W. Dixon.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2).

**BEESLEY, WILLIAM**, Binnyston Gardens, Bangalore City, Mysore, India. British. Works' Chemist. Took course in Bleaching and Dyeing at the Manchester College of Technology. Technological Certificate and Silver Medallist in Dyeing, City and Guilds of London Institute. Six years Chemist Assistant with Messrs. Binny & Co., Ltd. Now Head Chemist, Bangalore Woollen Mills, India. (*Signed by*) E. Knecht.

**BECKER, HOWARD**, 1510 Dana Ave., Cincinnati, Ohio, U.S.A. American.



Research Director for The R. I. Johnston Paint Co., Cincinnati, Ohio. Graduate student from Ohio Mechanics Institute, Cin., Ohio. 1 year graduate work, Columbia College, N.Y. 6 years teaching at Ohio Mechanics Institute and for 3 years head of the department. Member of the American Chemical Society, Society of Chemical Industry, German Chemical Society. (*Signed by*) John H. Foulger.

SMITH, ALEXANDER, P.O. Box 103, Nairobi, Kenya Colony. Scot. Chemist and Managing Director, A. H. Wardle & Co., Ltd. Lecturer on chemistry for 2 years, School of Mines, South Africa. Pharmaceutical Society, minor certificate. Consulting Chemist to Kenya Marble Quarries. In charge Hygiene Laboratory (Dr. Kochs), Dar-es-Salaam, 12 months. (*Signed by*) G. T. R. Francis.

## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS. British chemicals, their manufacturers and uses : being the official directory . . . containing a full list of members, with a classified list of British chemicals and a note of their industrial applications. London 1925. pp. 212. (*Reference.*) 10s. 6d. net.

From the Publishers : Messrs. Ernest Benn.

INDIAN CHEMICAL SOCIETY. Quarterly Journal. Vol. I, etc. Calcutta 1924 +. (Two copies.) From the Society.

INSTITUT INTERNATIONAL DE CHIMIE SOLVAY. Premier conseil de chimie, tenu à Bruxelles du 21 au 27 Avril 1922. Rapports et discussions . . . sur cinq questions d'actualité. Paris 1925. pp. xvi + 336. ill. (*Reference.*) 30 fr. net.

From the Publishers : MM. Gauthier-Villars & Cie.

NAMARI, ICHITARO. The electrolytic separation of magnesium from magnesia. Sakai 1924.. pp. iv + 160. ill. (*Recd.* 15/4/25.)

From the Author.

PHILIP, JAMES CHARLES. Physical chemistry : its bearing on biology and medicine. 3rd edition. London 1925. pp. viii + 368. ill. 8s. 6d. net. (*Recd.* 7/5/25.) From the Author.

RUMBOLD, W. G. Bauxite and aluminium. (Imperial Institute Monograph on Mineral Resources.) London 1925. pp. x + 110. ill. 6s. net. (*Recd.* 17/4/25.) From the Director.

SCIENTIFIC WORKER, The, and the B.A.C. Bulletin. Official organ of the National Union of Scientific Workers and the British Association of Chemists. New series. Vol. I, etc. London 1924 +. (*Reference.*)

From the Publishers : The National Union of Scientific Workers.

SPRING, WALTHER. Œuvres complètes, publiées par la Société Chimique de Belgique. 2 vols. Bruxelles 1914-1923. pp. iv + 900, iv, 901 to 1860. ill. 40 fr. (*Recd.* 9/4/25.)

From the Société Chimique de Belgique.

STAUDINGER, HERMANN. Introduction to qualitative organic analysis. Authorised translation by WALTER THEODORE KARL BRAUNHOLTZ. London 1925. pp. xvi + 112. 6s. 6d. net. (*Recd.* 8/4/25.) From the Publishers: Messrs. Gurney & Jackson.

TABLES ANNUELLES DE CONSTANTES et données numériques de chimie, de physique et de technologie. Vol. V. 1917-1922. Part i. Paris 1925. pp. xlii + 804. (*Reference.*)

From the Comité International.

THOMS, HERMANN. [Editor.] Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. III, Part ii. Vol. IV, Part i. Berlin 1925. pp. 289 to 544, 272. ill. M. 20. (*Recd.* 15/4/25.)

From the Publishers: Herren Urban & Schwarzenberg.

## II. By Purchase.

ANDERSON, ROBERT J. The metallurgy of aluminium and aluminium alloys. New York 1925. pp. xxxii + 914. ill. 42s. net. (*Recd.* 27/4/25.)

BABBITT, HAROLD E. Sewerage and sewage treatment. 2nd edition. New York 1925. pp. xvi + 516. ill. 25s. net. (*Recd.* 13/5/25.)

BRAGG, SIR WILLIAM HENRY, and BRAGG, WILLIAM LAWRENCE. X-rays and crystal structure. 5th edition. London 1925. pp. xii + 324. ill. 21s. net. (*Recd.* 13/5/25.)

BURRELL, GEORGE A. The recovery of gasoline from natural gas, with a discussion of motor fuels. New York 1925. pp. 600. ill. 35s. net. (*Recd.* 13/5/25.)

BURTON, ELI FRANKLIN. The physical properties of colloidal solutions. 2nd edition. London 1921. pp. viii + 222. ill. 12s. 6d. net. (*Recd.* 21/4/25.)

COFFIGNIER, CHARLES. Colours and varnishes. Translated from the French by A. HARVEY. London 1925. pp. viii + 258. ill. 12s. 6d. net. (*Recd.* 13/5/25.)

COLLOID SYMPOSIUM MONOGRAPH. Papers presented at the second National Symposium on Colloid Chemistry, June 1924. Edited by HARRY N. HOLMES. New York 1925. pp. viii + 368. ill. 25s. net. (*Recd.* 21/4/25.)

GOUGH, HERBERT JOHN. The fatigue of metals. London 1924. pp. xx + 304. ill. 25s. net. (*Recd.* 13/5/25.)

HATSCHEK, EMIL. [Editor.] The foundations of colloid chemistry; a selection of early papers bearing on the subject. Edited on behalf of the Colloids Committee of the British Association. London 1925. pp. 174. 18s. net. (*Recd.* 13/5/25.)

# PROCEEDINGS

OF THE

## CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, June 4th, 1925, at 8 p.m.,  
Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President,  
in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of Mr. Charles E. Soane, who was elected a Fellow on February 3rd, 1887, and who died on May 17th.

The PRESIDENT announced that the following address of congratulation had been sealed and will be presented on June 16th, 1925, to the Royal Institution on the occasion of the celebration of the Centenary of the discovery of benzene by Michael Faraday :

*To the President, Officers and Members of the Royal Institution  
of Great Britain.*

The Chemical Society welcomes the opportunity of associating itself with the Royal Institution in celebrating the centenary of the Discovery of Benzene by Michael Faraday, a discovery which was destined to have such far-reaching effects on the foundation and development of structural organic chemistry and to lead to the establishment of many new and important industries. We remember with pride that in 1868 the Chemical Society instituted a Triennial Lecture to commemorate the work of Faraday, for we recognise in him the pioneer of many of the principles underlying the chemical science of to-day.

We desire to join with the other Learned Societies and Academies of the world in offering our homage to the memory of this great and distinguished man.

Signed on behalf of the Chemical Society,

ARTHUR W. CROSSLEY, *President.*

JOCELYN THORPE, *Treasurer.*

T. SLATER PRICE, } *Secretaries.*

C. S. GIBSON, }

F. G. DONNAN, *Foreign Secretary.*

Sealed in Council this Fourth Day of June, One Thousand Nine Hundred and Twenty Five.

Mr. W. A. Wightman was formally admitted a Fellow of the Chemical Society.

Certificates were read for the first time in favour of :

William Bouch O'Brien Goudielock, 28, Fairfield Lane, Barrow-in-Furness.

Jnanendra Nath Ray, M.Sc., The University, Manchester.

Phyllis Mary Sanderson, 7, Cresswell Place, S.W. 10.

Eric Alfred Speight, B.Sc., A.R.C.S., 61, Arthur Road, Wimbledon Park, S.W. 19.

Gordon Mitchell Wright, M.A., B.Sc., University Chemical Laboratory, Cambridge.

The following papers were read :

"The spatial structure of *cycloparaffins*. Part I. A new aspect of Mohr's theory and the isomerism of decahydronaphthalene." By W. A. WIGHTMAN.

"Chenopodium oil. Part II. The hydrocarbon fraction." By T. A. HENRY and H. PAGET.

"Echitamine." By J. A. GOODSON and T. A. HENRY.

Ordinary Scientific Meeting, Thursday, June 18th, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT announced :

1. That, as Fellows would know, the Council has had before it for some time past the possibility of unifying chemical abstracts in pure and applied chemistry in the English language, and as stated in the Report of Council for 1923—1924, the Bureau of Chemical Abstracts was created to effect such unification. The Council, at its meeting that afternoon, had under consideration the following proposals of the Bureau, that

(1) The format adopted for the unified publications should be double column quarto.

(2) The type should be that now employed in the "A" Abstracts.

(3) The existing overlap, estimated to be at least 10%, should be eliminated,

as well as the further suggestion that, in the event of these proposals being adopted, one annual index covering both sections of the Abstracts should be supplied to all members of the two Societies concerned.

The Council has adopted the following resolution :

"That the Council concurs in the Bureau's proposals for the unification of the Abstracts in Pure and Applied Chemistry, and urges the Fellows, in the interests of co-operation and of

the consolidation of British Chemical Abstracts, to accept loyally such changes of format and arrangement as these proposals may involve."

It was further intimated that the proposals of the Bureau have also been accepted by the Council of the Society of Chemical Industry.

The President expressed the hope that Fellows would loyally support the efforts being made in the direction of unifying British chemical abstracts.

2. That the Faraday Society will hold a General Discussion on "Photochemical Reactions in Liquids and Gases" at Oxford on October 1st and 2nd next. The subject will be discussed under two main heads: (1) Einstein's Law of Photochemical Equivalence, (2) The Mechanism of Photochemical Reactions. Part I will be opened by Professor A. J. Allmand (King's College) and Part II by Professor M. Bodenstein (Berlin).

Fellows of the Chemical Society will be welcomed at this meeting, and it is hoped to accommodate all who attend the meeting at Exeter College and Lincoln College. Those desirous of attending are asked to communicate at once with the Secretary of the Faraday Society, 90, Great Russell Street, London, W.C. 1, from whom full particulars may be obtained.

3. That a communication has been received from the Committee of the van't Hoff Fund for the endowment of research in pure and applied chemistry. The amount from this fund available for distribution during 1926 is about 1400 Dutch florins.

A Committee, consisting of Professor A. F. Holleman (President), Professor F. M. Jaeger, Professor A. Smits, and Mr. J. P. Wibaut (Secretary), has been appointed to award Grants. Applications should be sent before November 1st, 1925, by registered post to: "Het Bestuur der Koninklyke Akademie van Wetenschappen, bestemd voor de Commissie van het 'van't Hofffonds,' Trippenhuis, Kloveniersburgwal, Amsterdam." Every applicant is requested to submit a detailed account of the manner in which he proposes to expend the grant and to state the reasons for which he makes his application.

Papers embodying the results of the research may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of papers containing the results of the research must be forwarded to the Committee.

4. That Volume V of the Annual Tables of Constants and Numerical Data is now ready, and is obtainable from Monsieur Charles Marie (9, Rue de Bagneux, Paris VI) who will be glad to send particulars on application.

Messrs. J. B. Reed and P. W. B. Harrison were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of :

Joseph Raymond Dolphin, B.Sc., Chemical Department, The University, Birmingham.

Henry Wilfrid Keenan, 80, Upper Richmond Road, East Sheen, S.W. 14.

Bertram Grey Leatherbarrow, Hill Crest, Station Road, Brimington, Chesterfield.

Henry Nicholson, M.Sc., Aberlady, Osborne Road, Stockton-on-Tees.

Robert Saxon, B.Sc., Westfield Terrace, Baildon, Yorks.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2) :

Bertram Cuthbert, c/o The British Australian Cotton Association, Ltd. Oil Mills, Brisbane.

Albert Louis Auguste Sigot, Institut de Chimie, 2, Rue Goethe, Strasbourg.

Mr. H. C. Sayer and Dr. H. Burgess were elected Scrutators, and a ballot for the election of Fellows was held, the following subsequently being declared elected as Fellows :

Marion Alice Battie, B.Sc., A.I.C.

Maung Hla Baw.

William Beesley.

William Ambler Berry, B.Sc.

Joseph John Blackie.

Samuel Cyril Blacktin, M.Sc.

Neville Melton Bligh, A.R.C.S., A.I.C.

Hugh Alexander Millar Borland, M.Sc., A.R.C.S.

Nirmal Boran Brohmachary, B.Sc.

Gertrude Margaret Bullick, B.Sc.

Ralph Edgar Cable.

Thomas Anthony Canning.

Leslie Marshall Clark, B.A., Ph.D., A.I.C.

Clive Kear Colwell, B.A.

Jan Coops.

William George Corderoy, B.Sc.

Oswald Pilkington Cronshaw.

John Carroll Culbert.

John Alexander Currie, B.A., B.Sc.

Alexander John Dey.

Thomas Dillon, M.A., D.Sc.

Octave Charles Marie Dony.

Howard Ecker.

Stanley James Featherston.

Malcolm Sinclair Gaskill.

William Edward Gibbs, D.Sc.

Norman Hamer, Assoc.M.C.T.

Ernest Hartshorne, B.Sc.Tech.

Arthur Harvey.

Charles Richard Hennings, Ph.D.

James Hindle.

Noel Waterman Vere Jones.

Frank William Linch, M.Sc., F.I.C.

Charles Lipshaw.

Thomas Moore, B.Sc.

Ivor Gray Nixon.

Vincent Joseph Occleshaw, M.Sc., A.I.C.

Ernest Charles Padgham.

James Arthur Prescott, M.Sc., A.I.C.

John Monteath Robertson, B.Sc., A.I.C.

Leon Rubenstein, B.Sc.

Malik Karam Singh, B.Sc.

Alexander Smith.

Norman Heath Smith, B.Sc.Tech.

Alec Thomas Streather, B.Sc., A.I.C.

John Thurgood, B.Sc.

Violet Corona Gwynne Trew.

Shojiro Uchida.

John Henry Walker, A.R.T.C., A.I.C.

Ernest Henry Warren, B.A.

James Watt.

William John Willis.

The following papers were read :

- "Investigations on the dependence of rotatory power on chemical constitution. Part XXVII. Some esters of *p*-toluene-sulphonic and sulphinic acids." By H. PHILLIPS.
- "The enhanced reactivity of newly formed molecules. Part I. The conversion of cyclols into ketones." By F. R. GOSS and C. K. INGOLD.
- "Constituents of *Myoporum laetum*, Forst ('The Ngaio'). Part I." By F. H. McDOWALL.
- "A synthesis of datisctetin." By J. KALFF and R. ROBINSON.
- "The relative directive powers of groups of the forms RO- and RR'N- in aromatic substitutions. Part IV. A discussion of the observations recorded in Parts I, II, and III." By J. ALLAN, A. E. OXFORD, R. ROBINSON, and J. C. SMITH.
- "A new aspect of the photochemical union of hydrogen and chlorine, and a quantitative study of the induction period." By R. G. W. NORRISH.

The Council has made the following Grants from the Research Fund :

	£	s.	d.
Bromination products of caronic acid. R. G. Atkinson. ...	12	0	0
Mechanism of tautomeric change. J. W. Baker ...	15	0	0
Photographic investigation of explosion waves. C. Campbell ...	5	0	0
Chemistry of the aminotriazole derivatives ( <i>contd.</i> ). P. K. Dutt. ...	5	0	0
Chemistry of the acridine molecule ( <i>contd.</i> ). P. K. Dutt ...	5	0	0
Ring-chain tautomerism. S. Dutt ...	10	0	0
Investigation and synthesis of ten-membered rings of the cryptopine type. G. A. Edwards ...	10	0	0
Contact electrification. F. Fairbrother ...	7	0	0
Oxidation of 5:6-benzo-1:1'-diethylcarbocyanine bromide. E. H. St. C. Flack ...	10	0	0
Oxidation of sesquiterpenes. D. T. Gibson ...	5	0	0
Action of thionyl chloride on hydroxybenzenes. A. Green ...	5	0	0
Structure of alkaloids and related compounds. J. M. Gulland... 10	10	0	0
Derivatives of methyl quinolines ( <i>contd.</i> ). D. L. Hammick ...	10	0	0
Some polarity effects in substituted stilbenes and tolanes. H. A. Harrison ...	10	0	0
Synthesis of alkaloids and allied compounds. R. D. Haworth ...	15	0	0
Investigation of the structure of Ciba Yellow ( <i>contd.</i> ). E. Hope ...	10	0	0
Experiments on the tetrahedral theory to S-N rings. R. F. Hunter ...	5	0	0
Action of aldehydes on aldehyde cyanohydrins in solution. B. H. Ingham ...	5	0	0
Reactivity of bivalent carbon. Mrs. E. H. Ingold ...	10	0	0
Correlation of additive reactions with tautomeric change ( <i>contd.</i> ). Mrs. E. H. Ingold ...	5	0	0
Mobility of the $\alpha\beta$ - $\beta\gamma$ change in unsaturated acids and unsaturated ketones. J. D. Johnson ...	15	0	0

	£	s.	d.
Influence of <i>gem</i> -dimethyl grouping on the formation and ring closure of substituted adipic acids. J. Kracovski ...	12	0	0
The constitution of strychnine and of brucine. F. Lions ...	20	0	0
Acid chlorides of the type chlorothiol benzoyl chloride and their products. E. W. McClelland ...	5	0	0
Influence of various substituents on the reactivity of organic compounds. I. Cyanohydrin formation. R. H. F. Manske...	10	0	0
Further investigation of the "Rotary Stillhead." J. E. Myers	10	0	0
Investigation of heterocyclic compounds related to tetrahydro-carbazole. S. G. P. Plant ...	15	0	0
Stereochemistry of arsenic. R. Raper ...	10	0	0
Rapid thermal decomposition of certain organic compounds under reduced pressure. J. Reilly ...	7	10	0
Ring-chain tautomerism of the $\beta\beta$ -disubstituted lævulic acids and their structures. E. Rothstein ...	20	0	0
(a) Substituted indole derivatives ...			
(b) Orientation in trisubstituted benzene derivatives ( <i>contd.</i> ). L. Rubenstein ...	5	0	0
Chemistry of the three-carbon system. L. F. Smith ...	12	0	0
Three-carbon tautomerism ( <i>contd.</i> ). E. A. Speight ...	15	0	0
The parachor and chemical constitution. S. Sugden ...	10	0	0
Influence of water vapour on reactions of the type: Solid $\rightleftharpoons$ solid + gas. B. Topley ...	5	0	0
Physical properties of straight-chain alkyl benzenes and their derivatives ( <i>contd.</i> ). E. E. Turner ...	5	0	0
Investigation of sulphur trioxide ( <i>contd.</i> ). I. Vogel ...	5	0	0
Synthetical experiments in the isoquinoline series. R. Campbell	10	0	0
Separation of platinum from iridium and rhodium with special reference to complex nitrites. D. F. Withers ...	10	0	0
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### PUBLICATIONS FUND.

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### LIST OF FELLOWS, 1925.

The List of Fellows for 1925 is now in active preparation and will be supplied to those Fellows who make application to the Assistant Secretary by the 31st July, 1925. In order that the new List may be as complete as possible, Fellows are invited to notify any change of address, or other alteration, before that date.

### BERICHTE, 1915-1924.

Sets of the Berichte from 1915 to 1924 (10 years) are now offered to Fellows of the Society at £22, carriage extra. Application should be made to Mr. S. E. Carr.

List of papers, or Abstracts thereof, received between May 22nd and June 18th, 1925. (This List does not include the titles of papers which have been read at a Scientific Meeting or which have appeared in the Journal.)

"A low voltage standard cell." By H. MASTIN.

"Hydrogen and oxygen electrode titrations of some dibasic acids and of dextrose." By H. T. S. BRITTON.

"Sulphur sesquioxide." By I. VOGEL and J. R. PARTINGTON.

"The relation of homogeneous to catalysed reactions. The catalytic decomposition of hydrogen iodide on the surface of gold." By C. N. HINSHELWOOD and C. R. PRICHARD.

"The decomposition of carbon monoxide in the corona due to alternating electric fields. Part I." By M. CRESPI and R. W. LUNT.

"The formation and stability of spiro-compounds. Part XII. Further evidence for the multiplanar configuration of the cycloheptane ring." By J. W. BAKER.

"The condensed ternary system phenol-water-salicylic acid." By C. R. BAILEY.

"The hydration of strong electrolytes and some properties of salt solutions." By J. N. SUGDEN.

"The action of sulphur on amines. Part III. *o*-, *m*-, and *p*-Chloro-anilines." By H. H. HODGSON and J. H. WILSON.

"The system sodium sulphite-sodium hydroxide-water." By D. L. HAMMICK and J. A. CURRIE.

- "Synthetical experiments in the isoquinoline group. Part V. Synthesis of substances allied to oxyberberine." By R. D. HAWORTH, W. H. PERKIN, and H. S. PINK.
- "Amino benzothiazoles. Part II. The naphthylamino naphthiazoles and their bromo derivatives." By R. F. HUNTER.
- "Negative adsorption: the surface tensions and activities of some aqueous salt solutions." By A. K. GOARD.
- "The structure of  $\alpha$ -campholytic acid. A correction." By J. P. C. CHANDRASENA, C. K. INGOLD, and J. F. THORPE.
- "The interaction of carbon dioxide and hydrogen on the surface of tungsten." By C. N. HINSHELWOOD and C. R. PRICHARD.
- "Note on potassium antimonoxalate." By L. H. A. HOLMES and E. E. TURNER.
- "Studies on the Walden inversion. Part IX. The influence of the solvent on the sign of the product in the conversion of  $\beta$ -bromo- $\beta$ -phenylpropionic acids to  $\beta$ -hydroxy- $\beta$ -phenylpropionamides." By G. SENTER and A. M. WARD.
- "'Co-ordination' and the periodic table." By I. AUCKEN.
- "Anode phenomena in the electrolysis of potassium ethyl malonate." By J. B. ROBERTSON.
- "The isomerism of the styryl alkyl ketones. Part II. The isomerism of the homologues of 2-hydroxystyryl, and of 3-methoxy-, and 4-hydroxy-styryl methyl ketones." By A. MCGOOKIN and D. J. SINCLAIR.
- "Hydrogen electrode studies of the precipitation of hydroxides. Part I. Magnesium, manganous, ferrous, cobalt, nickel, and thorium." By H. T. S. BRITTON.
- "Stereoisomeric azo-dyes." By G. T. MORGAN and D. G. SKINNER.
- "4- and 4'-Methoxybenzoylbenzoin." By H. GREENE.
- "The relative rates of conversion of phenoxyphenyldichloroarsine and its chloro-derivatives into chlorophenoxarsines." By E. ROBERTS and E. E. TURNER.
- "Chemistry of petroleum. Part II. The action of sodium hypochlorite on types of sulphur compounds found in petroleum distillates." By S. F. BIRCH and W. S. G. P. NORRIS.
- "Derivatives of  $\delta$ -o-aminobenzoylvaleric acid." By M. J. PATERSON and S. G. P. PLANT.
- "The action of formic acid on certain sesquiterpenes." By J. M. ROBERTSON, C. A. KERR, and G. G. HENDERSON.
- "Syntheses of disulphoxides." By D. T. GIBSON, C. J. MILLER, and S. SMILES.
- "The effect of gum arabic and other emulsifiers on the acid hydrolysis of esters in heterogeneous systems." By R. C. SMITH.
- "Lithium arc spectrum for polarimetric use." By P. C. AUSTIN.

- "Bismuth dihydride." By E. J. WEEKS and J. G. F. DRUCE.  
 "Reduction product of the hydroxyanthraquinones. Part VI." By A. G. PERKIN and G. YODA.  
 "A wandering of the acetyl group during methylation." By O. KUBOTA and A. G. PERKIN.  
 "The supposed formation of 1 : 2 : 4-oxadi-imine rings from nitroso-compounds and methylenearylamines." By G. N. BURKHARDT, A. LAPWORTH, and E. B. ROBINSON.  
 "The reaction of bromine with aliphatic acids. Catalytic effect of acyl halides." By H. B. WATSON.

## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

CLARKE, FRANK WIGGLESWORTH. The data of geochemistry. 5th edition. Washington 1924. pp. 842. (*Recd.* 26/5/25.)

From the Author.

DANIELS, GEORGE WILLIAM. Refrigeration in the chemical industry. London 1925. pp. x + 141. ill. (*Recd.* 29/5/25.)

From the Publisher : Mr. A. J. Rayment.

EASTMAN KODAK COMPANY. Abridged scientific publications from the Research Laboratories. Vol. VIII, 1924. Rochester, N.Y. 1925. pp. 156 + vi. ill. (*Reference.*)

From the Eastman Kodak Company.

IMPERIAL COLLEGE CHEMICAL SOCIETY. Journal. Vol. IV, containing the papers read during the session 1924—1925. London 1925. pp. 54. ill. (*Reference.*)

From the Society.

KLAR, M. The technology of wood distillation with special reference to the methods of obtaining the intermediate and finished products from the primary distillate. Translated [from the 2nd German edition] by ALEXANDER RULE. With an additional chapter by the translator. London 1925. pp. xvi + 496. ill. 25s. net. (*Recd.* 8/6/25.)

From the Publishers : Messrs. Chapman & Hall.

MORRICE, ALEXANDER. A treatise on brewing : wherein is exhibited the whole process of the art and mystery of brewing the various sorts of malt liquor ; with practical examples upon each species. Together with the manner of using the thermometer and saccharometer ; elucidated by examples, and rendered easy to any capacity, in brewing London porter [etc.]. London 1802. pp. [xii] + v to 180 + [xii]. ill. (*Reference.*)

From Dr. Alexander Scott.



NATIONAL BENZOLE ASSOCIATION and UNIVERSITY OF LEEDS.  
*Joint Benzole Research Committee*. Second report. London 1925.  
pp. 246. ill. (*Recd.* 18/5/25.)

From the National Benzole Association.

ORGANIC SYNTHESSES: an annual publication of satisfactory methods for the preparation of organic chemicals. Vol. IV. Edited by OLIVER KAMM [and others]. New York 1925. pp. viii + 90. 7s. 6d. net. (*Recd.* 22/5/25.)

From the London Publishers: Messrs. Chapman & Hall.

TIBA. *Revue Générale de Teinture Impression Blanchiment Apprêt et de Chimie Textile et Tinctoriale et Revue de la Soie Artificielle*. Year II, etc. Paris 1924 +. (*Reference.*)

From the Publishers.

## II. By Purchase.

BIRTWHISTLE, GEORGE. The principles of thermodynamics. Cambridge 1925. pp. x + 164. ill. 7s. 6d. net. (*Recd.* 10/6/25.)

CHEMICAL ENGINEERING AND CHEMICAL CATALOGUE 1925: a catalogue of heavy and fine chemicals, raw material, machinery, plant and equipment applicable to production industries. Compiled with the co-operation of leading British manufacturers by LEONARD HILL. Edited by DUDLEY MAURICE NEWITT. London 1925. pp. 260. ill. (*Reference.*) 21s. net.

DUKES, CUTHBERT. The bacteriology of food. London 1925. pp. xii + 180. ill. 7s. 6d. net. (*Recd.* 10/6/25.)

FRIEND, JOHN NEWTON. [Editor.] A text-book of inorganic chemistry. Vol. III. Part i. The alkaline earth metals. By MAY SYBIL BURR (née LESLIE). London 1925. pp. xxvi + 346. (*Reference.*) 20s. net.

HOWE, H. E. [Editor.] Chemistry in industry: a coöperative work intended to give examples of the contributions made to industry by chemistry. New York 1924. pp. xiv + 372. ill. 6s. net. (*Recd.* 16/4/25.)

JÖRGENSEN, ALFRED. Micro-organisms and fermentation. 5th edition. Revised by the Author with the assistance of S. H. DAVIES. London 1925. pp. xiv + 468. ill. 30s. net. (*Recd.* 10/6/25.)

JOHNSON, J. B. Materials of construction. Rewritten by M. O. WITHEY and JAMES ASTON. Edited by F. E. TURNAURE. 6th edition. New York 1925. pp. xx + 866. ill. 30s. net. (*Recd.* 13/5/25.)

KLOOSTER, HENRY S. VAN. Lecture and laboratory experiments in physical chemistry. 2nd edition. Easton, Pa. 1925. pp. x + 274. ill. 12s. net. (*Recd.* 15/5/25.)

LADOO, RAYMOND B. Non-metallic minerals: occurrence—preparation—utilization. New York 1925. pp. viii + 686. ill. 30s. net. (*Recd.* 10/6/25.)

LORD, LEONARD J. Practical butter and cheese making. London 1925. pp. 200. ill. 10s. 6d. net. (*Recd.* 13/5/25.)

MELLOR, JOSEPH WILLIAM. Modern inorganic chemistry. New edition. London 1925. pp. xx + 1104. ill. 12s. 6d. net. (*Recd.* 15/5/25.)

NEWMAN, FRANK HERBERT. The production and measurement of low pressures. London 1925. pp. 192. ill. 16s. net. (*Recd.* 10/6/25.)

NORTH, SYDNEY H., and GARBE, J. B. Low temperature distillation, home oil supply and the utilization of "waste" coal. London 1925. pp. vi + 216. ill. 15s. net. (*Recd.* 13/5/25.)

O'BRIEN, W. B. Factory practice in manufacture of azo dyes. Easton, Pa. 1924. pp. viii + 176. ill. 22s. 6d. net. (*Recd.* 16/4/25.)

PARRY, ERNEST JOHN. Parry's cyclopædia of perfumery. 2 vols. London 1925. pp. vi + 840. (*Reference.*) 36s. net.

RICHMOND, HENRY DROOP. The laboratory book of dairy analysis. 3rd edition. London 1925. pp. viii + 118. ill. 5s. net. (*Recd.* 15/5/25.)

SIM, JAMES. Steam condensing plant in theory and practice. London 1925. pp. xiv + 272. ill. 18s. 6d. net. (*Recd.* 10/6/25.)

THOMPSON, MAURICE DE KAY. Theoretical and applied electrochemistry. Revised edition. New York 1925. pp. xx + 552. ill. 20s. net. (*Recd.* 13/5/25.)

THOMSON, SIR JOSEPH JOHN. The electron in chemistry: being five lectures delivered at the Franklin Institute, Philadelphia. [Philadelphia] 1923. pp. vi + 144. ill. 10s. 6d. net. (*Recd.* 15/5/25.)

VEDDER, EDWARD B. The medical aspects of chemical warfare. With a chapter on the naval medical aspects of chemical warfare by DUNCAN C. WALTON. Baltimore 1925. pp. xvi + 328. ill. 32s. 6d. net. (*Recd.* 26/5/25.)

WELLS, HARRY GIDEON. The chemical aspects of immunity. New York 1925. pp. 254. 20s. net. (*Recd.* 18/5/25.)

WILLIAMS, GEORGE BRANSBY. Sewage disposal in India and the East. Calcutta 1924. pp. x + 230. ill. 17s. 6d. net. (*Recd.* 13/5/25.)

WOOD, THOMAS BARLOW. Animal nutrition. London 1924. pp. viii + 226. 4s. 6d. net. (*Recd.* 15/5/25.)

WORLD POWER CONFERENCE, First. London 1924. Transactions. 5 vols. London [1925]. pp. xxiv + 1506, xviii + 1600, xvi + 1502, xx + 1816. (*Reference.*)

# PROCEEDINGS

## OF THE

### CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, October 15th, 1925,  
at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S.,  
President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society,  
through death, of the following Fellows :

	<i>Elected.</i>	<i>Died.</i>
Richard Burtles.....	May 3rd, 1923.	July 3rd.
Charles Frederick Chandler .....	Feb. 1st, 1872.	Aug. 25th.
William Henry Deering .....	April 1st, 1869.	Sept. 5th.
William Joseph Dibdin .....	April 15th, 1880.	June 8th.
Samuel Jackson.....	Dec. 15th, 1892.	July 27th.
Francis Robert Japp .....	Feb. 6th, 1879.	Aug. 1st.
Reginald A. Joyner .....	Dec. 6th, 1917.	Oct. 8th.
Daniel Rankin Steuart .....	Dec. 15th, 1881.	Aug. 1st.
Leonard E. Vlies .....	Feb. 21st, 1918.	July 26th.

The PRESIDENT announced that :

1. The first of the two Informal Lectures to be held this Session  
will be delivered in the Rooms of the Society on Thursday,  
November 26th, 1925, by Professor R. Robinson, D.Sc., F.R.S.,  
who has chosen as his subject :

“Recent Researches on the Structural Relationships of  
Some Plant Products.”

Special attention is drawn to the fact that the lecture will be  
delivered at 6 o'clock instead of at 8 o'clock as stated on the meeting  
card.

2. Following the innovation made in October, 1923, it has  
been decided to hold next month a united dinner for British Chemists.  
The dinner, to be called “British Chemistry Dinner” is under the  
auspices of the Chemical Society, the Institute of Chemistry, the  
Society of Chemical Industry, the Association of British Chemical  
Manufacturers, the Institution of Petroleum Technologists, the  
Society of Public Analysts, the Bio-Chemical Society, the Oil and  
Colour Chemists' Association, and the Chemical Industry Club,

and will be held at the Connaught Rooms, Great Queen Street, W.C. 2, on Friday, November 13th, 1925, at 6.30 for 7 p.m. Dr. W. R. Ormandy, Chairman of the Chemical Industry Club, will preside.

The price of the tickets is 15s. each (not including wine) for lady or gentleman, and as the accommodation is limited to about 400, early application is advisable.

Besides the Loyal Toasts, there will be only two other Toasts, namely, "The Profession and Industry of Chemistry" and "The Guests." After dinner, there will be dancing and musical items.

Application for tickets (15s. each), with remittance, should be sent to the Secretary of the Chemical Industry Club, 2, Whitehall Court, S.W. 1.

3. The Selection Committee of the Harrison Memorial Prize will meet shortly to consider the award of the Harrison Prize.

The Prize, of the value of about £150, is to be awarded to the chemist of either sex being a natural born British subject and not at the time over thirty years of age, who, in the opinion of the Selection Committee, during the previous five years has conducted the most meritorious and promising original investigations in any branch of pure or applied chemistry and published the results of those investigations in a scientific periodical or periodicals.

Provided that in the opinion of the Selection Committee there is a candidate of sufficient distinction to warrant an award of the Prize, the award is to be made in December, 1925.

The Selection Committee is prepared to receive applications, nominations or information as to candidates eligible for the Prize. Any such information must be received by The President, The Chemical Society, Burlington House, Piccadilly, W. 1, not later than Tuesday, December 1st, 1925.

4. As Fellows are already aware, the Council has approved the proposals of the Bureau of Chemical Abstracts (see Procs. for June, 1925), aiming at the unification of abstracts of chemical papers in this Country. As a consequence of the arrangements made, "British Chemical Abstracts" will appear as from January, 1926, in two sections, namely, A (Pure Chemistry) and B (Applied Chemistry), and will be in the same format and type, without overlap, and with one common index at the end of the year. The format adopted is that at present employed for the "B" Abstracts; beginning, therefore, with January, 1926, Fellows will receive the Abstracts in Pure Chemistry in quarto double-column size. This clearly means a break with the past, so far as the Chemical Society is concerned, but the Council trusts that in the interests of co-operation the Fellows will accept these changes with loyalty.

5. The price of the Annual Reports for 1925, Vol. XXII, will be the same as for Vol. XXI, namely 5s. 6d. post free to those Fellows who apply by Christmas Day, 1925. Application should be made to the Assistant Secretary, and must be accompanied by a remittance for 5s. 6d.

6. Volume I of the Memorial Lectures has been reproduced by a photographic process, and is now on sale at the Publishers, Messrs. Gurney & Jackson, 33, Paternoster Row, E.C. 4, price to Fellows 9s. post free.

7. Sets of the *Berichte* from 1915-1924 (10 years) can be obtained on application to the Assistant Secretary at the reduced price of £22, plus carriage.

8. In continuance of the arrangement made with the American Chemical Society, the *Journal of the American Chemical Society*, *Industrial and Engineering Chemistry*, and *Chemical Abstracts*, can be obtained by Fellows at the following reduced rates :

Price for any one journal \$7.25, post free,

Price for any three journals \$17.50, post free,

while *Chemical Reviews* is offered to Fellows at \$4.50, post free. Applications should be made as soon as possible to Dr. Charles L. Parsons, Secretary, American Chemical Society, 1709, G. Street N.W., Washington, D.C., U.S.A.

The *Journal of Physical Chemistry* is obtainable by Fellows at \$8.00 post free, published at \$10.00. Application should be made to the *Journal of Physical Chemistry*, Ithaca, N.Y., U.S.A.

9. A meeting of the Research Fund Committee will be held in December next. Applications for Grants, to be made on forms obtainable from the Assistant Secretary, must be received on or before Tuesday, December 1st, 1925. Applications from Fellows will receive prior consideration.

All persons who received Grants in December, 1924, or in December of any previous year, whose accounts have not been closed by the Council, are reminded that Reports must be returned by December 1st.

The following were formally admitted Fellows of the Chemical Society : G. M. Bullick, C. G. Trew, I. C. P. Smith, W. G. Corderoy, E. H. Warren, I. A. Smith, C. F. Flint, R. R. Garrahan, N. M. Bligh, and E. C. Padgham.

Certificates were read for the first time in favour of :

Robert Leslie Andrew, Dominion Laboratory, Wellington, New Zealand.

Louis Baissac, Curepipe Road, Mauritius.

William Francois Barker, Ph.D., Rhodes University College, Grahamstown, S. Africa.

Ralph Basden, The Technical College, Newcastle, N.S.W.

Frank Bell, 11, Edwy Parade, Gloucester.

Arthur Neville Copnall Bennett, B.Sc., 27, Dale Road, Luton.

John Cecil Bird, B.Sc., A.I.C., 72, Dyne Road, Kilburn, N.W. 6.

Lionel Christopher William Birkett, B.Sc., Moor House, North Road, Spenny-moor.

James Boyd, F.I.C., P.O. Box 1162, Johannesburg.

Frank Symonds Bradhurst, c/o Messrs. Holbrooks, Ltd., Danks Street, Waterloo, Sydney.

John Hildred George Carlile, B.Sc., A.R.C.S., 29, Orlando Road, Clapham, S.W. 4.

Leslie James Chalk, B.Sc., 14, Shrubbery Road, Southall.

Rama Charan, B.Sc., B.Sc.Tech., 12, Bank Road, Allahabad.

Edward Mortimer Crowther, D.Sc., F.I.C., Rothamsted Experimental Station, Harpenden, Herts.

Frank Edwin Dickinson, Research Establishment, Sutton Oak, St. Helens.

William Donovan, M.Sc., Dominion Laboratory, Wellington, New Zealand.

John Stanley Dunn, M.A., Ph.D., A.I.C., 39, Victoria Park, Cambridge.

Edwin Francis Edwards, c/o Messrs. Holbrooks, Ltd., Waterloo, Sydney.

John Moelwyn Edwards, 92, Jamaica Road, Rotherhithe, S.E. 16.

James Walter Shanks Gemmell, B.Sc., Helen's Villa, Fleming Place, St. Andrews.

Francis Reginald Glover, 98/100, St. Peters Street, Nottingham.

Felix John Theodore Grigg, M.Sc., A.I.C., Government Buildings, Christchurch, New Zealand.

John Hall, M.Sc., A.I.C., 202, Burton Road, Derby.

Herbert Sim Hirst, B.Sc., Trinity College, Cambridge.

Toru Iwadare, c/o Banyu Pharmaceutical Co., Ltd., 174, Shimomeguro, Tokyo, Japan.

David Christopher Mendis Jayewardene, Fern Bank, Moratuwa, Ceylon.

Charles Benjamin Johnson, 134, Preston New Road, Blackburn.

Walter Idris Jones, Ph.D., B.Sc., 7, Manor Street, Cambridge.

Charles King, 141, Bath Street, Glasgow.

Frederick Karl Victor Koch, B.Sc., A.R.C.S., 9, Crossfield Road, Hampstead, N.W. 3.

Charles Dudley Langford, B.Sc., A.R.C.S., 43, Ashbourne Avenue, Temple Fortune, N.W. 11.

Henry Guinness de Laszlo, B.A., Ph.D., 3, Fitzjohn's Avenue, Hampstead, N.W. 3.

Sam Lenher, B.A., 15, Gordon Street, W.C. 1.

William Macartney, c/o Messrs. Grattan & Co., Ltd., Belfast.

William Francis Martin, F.I.C., 27, Shandon Crescent, Edinburgh.

Arthur Moore, Highfield, Oakworth, Keighley.

John Blackburn Murgatroyd, 90, St. George's Square, S.W. 1.

Chitsukhlal Hiralal Nanavati, 80, Esplanade Road, Fort, Bombay.

Anna Maria O'Mara, 83, Elsham Road, Holland Park, W. 14.

Norman Frederick Parker, B.A., A.I.C., 45, Sellons Avenue, Harlesden, N.W. 10.

Marjorie Ellen Pring, B.Sc., 66, St. Augustine's Avenue, S. Croydon.

Herbert Charles Roberts, 15, Estcourt Terrace, Headingley, Leeds.

George Baty Scott, 37, Woodbridge Road, Knowle, Bristol.

Rupert Boswood Scammell, B.Sc., c/o Messrs. F. H. Faulding & Co., Ltd., Castlereagh Street, Redfern, Sydney.

Ugo Shin, Agricultural Farm, Mandalay.

Dalip Singh, Ph.D., near Tehsil P.O., Lahore.  
 William Veale Thorpe, B.A., 270, Balham High Road, S.W. 12.  
 William Milburn Towler, B.Sc., 28, Denton Avenue, Roundhay, Leeds.  
 David Traill, B.Sc., 58, Chalmers Street, Dunfermline.  
 Donald Morrison Turner, 40-42, Lexington Street, W. 1.  
 Geoffrey Turner, B.Sc., 85, Winchester Avenue, Leicester.  
 Frederick Henry Webb, St. Malo, Jameson Road, Harpenden, Herts.  
 Hugh Amphlett Williams, 249, Kennington Road, S.E. 11.  
 Robert Harding Williams, 131, Anlaby Road, Hull.  
 John James Benjamin Wolfe, 24, Greyhound Road, Hammersmith, W. 6.  
 John Frederick Zimmermann, 17, Stile Hall Gardens, Chiswick, W. 4.

The following papers were read :

- "The effect of ultra-violet light on dried hydrogen and oxygen." By H. B. BAKER and M. CARLTON.
- "A new per-oxide of barium." By M. CARLTON.
- "The production of oxide-films on copper at ordinary temperatures." By U. R. EVANS.
- "The structural isomerism of the oximes. Part III. The benzilmonoximes." By A. H. ATTACK and F. W. ATTACK.

List of papers, or abstracts thereof, received between June 18th and October 15th, 1925. (This list does not include the titles of papers which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

- "The action of sulphuretted hydrogen on a neutral solution of potassium permanganate." By H. B. DUNNICLIFF and S. DAYAL.
- "Note on the preparation of thiocarbonyl." By S. J. C. SNEDKER.
- "Studies with the microbalance. Part II. The photochemical decomposition of silver chloride." By E. J. HARTUNG.
- "Preparation, hydrolysis and reduction of the isomeric fluorobenzyl bromides." By J. B. SHOESMITH and R. H. SLATER.
- "The action of silica on electrolytes. Part II." By A. F. JOSEPH and H. B. OAKLEY.
- "The formation and growth of silver nuclei in the decomposition of silver oxalate." By J. Y. MACDONALD and C. N. HINSHELWOOD.
- "Researches in the menthone series. Part I." By J. READ and A. M. R. COOK.
- "Studies in adsorption by the application of optical methods. Fixation by dispersoids of methylene-blue within the disperse phase." By A. FODOR and R. RIWLIN.
- "The physical chemistry of the metal-ammonium complexes. Part I. The blue of the copper-ammonium complexes." By S. S. BHATNAGAR, M. PRASAD and D. NATH.
- "The correlation of absorption spectra with ionisation in violuric acid." By R. A. MORTON and A. H. TIPPING.
- "Absorption spectra and lactam-lactim tautomerism." By R. A. MORTON and E. ROGERS.
- "The heat of combustion of salicylic acid." By E. BERNER.

- "An electrometric and phase rule study of some basic salts of copper." By H. T. S. BRITTON.
- "The distribution of pyridine between water and benzene." By R. M. WOODMAN and A. S. CORBET.
- "The velocity of decomposition of oxalic acid in solution." By D. L. WATSON.
- "The absorption of gases in colloidal solutions." By A. GATTERER.
- "A circulation apparatus for gases." By N. G. CHATTERJI and G. I. FINCH.
- "2:4-Dinitrophenylhydrazine as a reagent for aldehydes and ketones." By O. L. BRADY and G. V. ELSMIE.
- "The methylation of the oximes of benzil." By O. L. BRADY and H. M. PERRY.
- "The alkaline oxidation of some carbohydrates by means of dyestuffs, considered quantitatively." By E. KNECHT and E. HIBBERT.
- "Unstable states of solutions of sodium behenate." By M. E. LAING and collaborators.
- "Note on the preparation of *p*-nitrophenylhydrazine." By H. H. HODGSON and H. G. BEARD.
- "The preparation of 2-nitro-1-halogen naphthalenes and of  $\beta$ -nitronaphthalene." By H. H. HODGSON and E. KILNER.
- "The swelling and dispersion of some colloidal substances in ether-alcohol mixtures." By E. W. J. MARDLES.
- "The relationship of salts in dilute aqueous solution as determined by their influence on the critical solution temperature of the system phenol-water." By J. H. CARRINGTON, L. R. HICKSON, and W. H. PATTERSON.
- "The colorimetric dissociation constants of dinitrocatechol and dinitroresorcinol." By F. C. LAXTON, E. B. R. PRIDEAUX, and W. H. RADFORD.
- "The cyanine dyes. Part IX. The mechanism of the condensations of quinaldine alkylidides in presence of bases." By W. H. MILLS and R. RAPER.
- "Dibenzylquinaldine." By W. H. MILLS and A. T. AKERS.
- "The action of nitrous acid upon amides and other 'amino' compounds." By R. H. A. PLIMMER.
- "Olefinic terpene ketones from the volatile oil of flowering *Togetes glandulifera*. Part I." By T. G. H. JONES and F. B. SMITH.
- "On the interaction between copper and sulphuric acid." By C. W. ROGERS.
- "Trypanocidal action and chemical constitution. Part II. Arylamides of 4-aminophenyl-arsinic acid." By H. KING and W. O. MURCH.
- "The butyl esters of the simpler amino-acids. Part I." By W. T. J. MORGAN.
- "The influence of salts in ethyl alcohol solution on the mutual miscibility temperature of the system ethyl alcohol-paraffin." By E. J. HOWARD and W. H. PATTERSON.
- "Condensations of the sodium derivatives of trimethylene glycol and glycerol." By A. FAIRBOURNE and G. E. FOSTER.
- "An investigation of the effect of differential aëration on corrosion by means of electrode potential measurements." By A. L. McAULAY and F. P. BOWDEN.
- "The recognition of allotropy in metals." By D. STOCKDALE.
- "Solubility influences. Part I. The effect of some salts, sugars, and temperature on the solubility of ethyl acetate in water." By S. GLASSTONE and A. POUND.
- "Experiments on the synthesis of apofenchocamphoric acid. Preparation of  $\alpha$ -dimethyl- $\beta'$ -carboxyadipic acid." By K. C. ROBERTS.



- "Electrometric study of the reactions between alkalis and silver nitrate solutions." By H. T. S. BRITTON.
- "Electrometric separation of the iodide, bromide and chloride of silver." By H. T. S. BRITTON.
- "Reduction products of the hydroxyanthraquinones. Part VII." By W. B. MILLER and A. G. PERKIN.
- "Chloro-derivatives of *m*-hydroxybenzaldehyde." By H. H. HODGSON and H. G. BEARD.
- "The nitration of *m*-bromophenol." By H. H. HODGSON and F. H. MOORE.
- "The reduction of arsenic compounds by sodium hyposulphite. The production of subsulphides of arsenic." By W. FARMER and J. B. FIRTH.
- "The electrical conductivities of hydrochloric acid and potassium chloride in water and acetone-water mixtures." By T. K. BROWNSON and F. M. CRAY.
- "Metalloccyclic compounds. Part I. Compounds of tellurium." By H. D. K. DREW.
- "The action of hydrogen fluoride on compounds of selenium and tellurium. Part I. Selenium dioxide." By E. B. R. PRIDEAUX and J. O'N. MILLOTT.
- "The resolution of an asymmetric arsenic compound into its optically active forms." By W. H. MILLS and R. RAPER.
- "The electrical conductivity of phosphorus pentachloride." By G. W. F. HOLROYD, H. CHADWICK, and J. MITCHELL.
- "Hydrogen electrode studies of the precipitation of basic chromates, borates and carbonates." By H. T. S. BRITTON.
- "The relation between chemical constitution and pungency in acid amides." By E. C. S. JONES and F. L. PYMAN.
- "The rate of reaction of bromine with aqueous formic acid." By D. L. HAMMICK, W. K. HUTCHISON and F. R. SNELL.
- "The quaternary salts of benzoxazoles." By L. M. CLARK.
- " $\gamma\gamma'$ -Dichloropropyl sulphide." By G. M. BENNETT and A. L. HOCK.
- "Synthesis in the thianthren series. Part II." By M. SEN and J. N. RAY.
- "Some lactonic esters derived from phenacyl bromide by condensation with ethyl sodiomalonate and analogous substances." By R. M. RAY and J. N. RAY.
- "The velocity of decomposition of heterocyclic diazonium salts. Part I. Diazonium salts of the pyrazole and pyrazolone series." By J. REILLY and D. MADDEN.
- "Orientating effects in the diphenyl series." By H. G. DENNETT and E. E. TURNER.
- "The relative directive influence of polar and steric effects on ring closure." By R. W. J. SMITH and E. E. TURNER.
- "The configuration of the ammonium ion." By W. H. MILLS and E. H. WARREN.
- "Symmetrical substitution derivatives of trimethylene bromide and penta-methylene bromide." By W. H. MILLS and L. BAINS.
- "Further studies on a new chlorinating agent preparation of polychloro-derivatives of toluene." By O. SILBERRAD.
- "The equilibrium in the systems aluminium sulphate-copper sulphate-water and aluminium sulphate-ferrous sulphate-water at 25°." By V. J. OCCLESIAHAW.
- "Reactions of the meso-hydroxyanthrones." By M. A. MATTHEWS.

- "The influence of different nuclei on the absorption spectra of substances." By J. E. PURVIS.
- "The occurrence of sylvestrene." By B. S. RAO and J. L. SIMONSEN.
- "The partial formaldehyde vapour pressures of aqueous solutions of formaldehyde. Part II." By W. LEDBURY and E. W. BLAIR.
- "Trypanocidal action and chemical constitution. Part III. Arsinic acids containing the glyoxaline nucleus." By I. E. BALABAN and H. KING.
- "The preparation of tertiary arsines by the Friedel-Crafts reaction." By A. F. HUNT and E. E. TURNER.
- "Equilibrium in the system:  $\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$ ." By G. J. BURROWS.
- "The parachor and chemical constitution. Part III. Orientation isomerism in aromatic compounds." By S. SUGDEN and H. WILKINS.
- "The aluminioxalates of some optically active bases." By T. B. CHILD, E. ROBERTS, and E. E. TURNER.
- "On the equilibrium between methylformate, methanol and hydrogen, and some related equilibria." By J. A. CHRISTIANSEN.
- "Hydrogen electrode studies of the reactions between solutions of salts of weak metallic bases and the acetate, oxalate and tartrate of sodium, with a note on the effect of dextrose on zirconium chloride solution." By H. T. S. BRITTON.
- "The conversion of *r*-phenyl- $\alpha$ -naphthyl-glycollic acid into ketones." By A. MCKENZIE and H. J. TATTERSALL.
- "Studies of equilibrium in systems of the type  $\text{Al}_2(\text{SO}_4)_3\text{-M''SO}_4\text{-H}_2\text{O}$ . Part II. Aluminium sulphate-nickel sulphate-water at 30°." By R. M. CAVEN and T. C. MITCHELL.
- "The system silver sulphate-aluminium sulphate-water at 30°." By R. M. CAVEN and T. C. MITCHELL.
- "Change of crystal habit of some salts when crystallised from silicic acid gel." By H. A. FELS and J. B. FIRTH.
- "The ionic activity product of water in glycerol-water mixtures." By J. COLVIN.
- "2-*m*-Xylidino-5-ethoxy-4:5-dihydrothiazole." By V. K. NIMKAR and F. L. PYMAN.
- "The change in the absorption spectra of aromatic nitro-compounds in liquid ammonia with time." By W. E. GARNER and H. F. GILLBE.
- "Nitrosyl sulphuric acid. Part I." By G. A. ELLIOTT, L. L. KLEIST, and H. W. WEBB.
- "The action of acetylenetetra-bromide on organic bases." By J. D. FULTON.
- "Production of *cyclotelluripentanedionedichlorides*." By G. T. MORGAN (with F. J. CORBY, O. C. ELVINS, E. JONES, R. E. KELLETT, and C. J. A. TAYLOR).
- "Interactions of tellurium tetrachloride and monoketones." By G. T. MORGAN and O. C. ELVINS.
- "A note on the sulphonation of 4-chloro-phenol." By J. M. GAUNTLETT and S. SMILES.
- "Some analogues of adrenalone. Part I." By F. MATTHEWS.
- "The relationship between the optical rotatory powers and the relative configurations of optically active compounds. Part II. The relative configurations of the optically active mandelic acids and  $\beta$ -phenyl-lactic acids." By G. W. CLOUGH.
- "Synthesis of 2:3:5-trimethyl glucose." By J. C. IRVINE and J. W. H. OGDEN.

- "The oxidation of certain sesquiterpenes with chromyl chloride and chromic acid." By D. T. GIBSON, J. M. ROBERTSON, and J. SWORD.
- "Tesla-luminescence spectra. Part VI. Some amino-derivatives." By W. H. McVICKER, J. K. MARSH, and A. W. STEWART.
- "Glyceryl glucoside." By H. S. GILCHRIST and C. B. PURVES.
- "A comparison of methods of measuring the polarity of surfaces." By N. K. ADAM, R. S. MORRELL, and R. G. W. NORRISH.
- "cycloHexanespirocyclohexane." By W. S. G. P. NORRIS.
- "The effect of heat on chloral hydrate." By J. D. MOUNFIELD and J. K. WOOD.
- "The solubilities of sodium, potassium and calcium ferrocyanides. Part I." By M. P. APPLEBEY and M. FARROW.
- "Isomeric change of aromatic compounds. Part I. The conversion of diacylanilides into acylaminoketones." By A. W. CHAPMAN.
- "Nitrosyl sulphuric acid." By F. J. WILSON and H. W. WEBB.
- "The constitution of the metallic ozonides." By E. C. C. BALY and R. W. RIDING.
- "The influence of substituents on the stability of Schiff's bases. Part I. Hydrolysis of nitro- and methoxy-benzylidene anilines." By E. M. LANGMAN, W. HEALEY, and P. K. DUTT.

## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

ABDERHALDEN, EMIL. [Editor.] Handbuch der biologischen Arbeitsmethoden. Abt. I, Chemische Methoden, Teil 6, Heft. iii, Abt. III, Physikalisch-chemische Methoden, Teil A, Heft v. Berlin 1925. pp. [268] + xxiv, [136]. ill. *M.* 12.30, *M.* 5.70. (*Recd.* 12/9/25.) From the Publishers: Herren Urban & Schwarzenberg.

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BERRY, ARTHUR JOHN. Volumetric analysis: with a chapter on simple gravimetric determinations. 3rd edition. Cambridge 1925. pp. viii + 152. ill. 9s. net. (*Recd.* 9/10/25.)

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1919-22. (Report to the Accessory Food Factors Committee appointed jointly by the Medical Research Council and the Lister Institute.) London 1923. pp. 230 + 13 plates. 7s. 6d. net.

MEDICAL RESEARCH COUNCIL. Special Report Series, No. 91. An investigation of the Salmonella group, with special reference to food poisoning. By WILLIAM GEORGE SAVAGE and P. BRUCE WHITE. London 1925. pp. 160. 3s. 6d. net.

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— Special Report Series, No. 93. Experimental rickets: the effect of cereals and their interaction with other factors of diet and environment in producing rickets. By EDWARD MELLANBY. London 1925. pp. 66 + 40 plates. 3s. 6d. net.

From Professor J. C. Drummond.

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From Professor B. N. Menschutkin.

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PLIMMER, ROBERT HENRY ADERS, and PLIMMER, VIOLET G. Food and health. London 1925. pp. vi + 64. ill. 3s. 6d. net. (Recd. 15/10/25.)

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ZSIGMONDY, RICHARD. Kolloidchemie. Ein Lehrbuch. 5th edition. I. Allgemeiner Teil. (Chemische Technologie in Einzeldarstellungen.) Leipzig 1925. pp. xii + 246. ill. *Gm.* 11. (*Recd.* 31/7/25.) From the Publisher: Herr Otto Spamer.

## II. By Purchase.

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HISTORY OF THE GREAT WAR. Medical Services. Vol. II. Including . . . gas warfare, and gas poisoning in tanks and mines. Edited by SIR WILLIAM GRANT MACPHERSON [and others]. London 1923. pp. viii + 622. ill. 25s. net. (*Recd.* 20/6/25.)

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## III. Pamphlets.

## (a) From Professor P. Phillips Bedson.

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FERNANDES, FRANCIS VITO. The Indian school of Chemistry. The researches of Professor Ray and his pupils at Presidency College. (From the *Presidency College Magazine*, 1915, 1.)

FRENCH COMMISSION ON THE USE OF EXPLOSIVES IN THE PRESENCE OF FIRE-DAMP IN MINES. Report. Translated by W. J. BIRD and M. WALTON BROWN. 3 parts. Newcastle-upon-Tyne 1890-91. pp. 164. ill.

MOREWOOD, A. PALMER. Shaw's gas tester, for detecting the presence of small percentages of gas in colliery workings. London 1896. pp. 18. ill.

NORTH OF ENGLAND INSTITUTE OF MINING AND MECHANICAL ENGINEERS. Report of the Committee appointed to enquire into the explosion of an air receiver at Ryhope Colliery. (From the *Trans. N. England Inst. Min. & Mech. Eng.*, 1888, 37.) ill.

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— On nitrosopinene. London 1898. pp. 19.

TROBRIDGE, FREDERICK GEORGE. Über die Ester- und Amid-Sauren der Itaconsäure. Beuel a. Rh. 1910. pp. 36.

## (b) Miscellaneous.

ANDERSON, L. A. P., HOWARD, ALBERT, and SIMONSEN, JOHN LIONEL. Studies on lathyrism. I. (From the *Indian J. Med. Research*, 1925, 12.)

GORTNER, ROSS AIKEN, and HOFFMAN, WALTER FRED. Quantitative estimation of chlorides and sulphates in expressed plant tissue fluids. (From the *Bot. Gaz.*, 1924, 77.)

HENDRICK, JAMES. Some characters of Scottish soils. (From the *Trans. Highland & Agric. Soc. of Scotland*, 1925.)

MASON, FREDERICK ALFRED. An introduction to the literature of chemistry for senior students and research chemists. Oxford 1925. pp. 42.

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— Paper No. 8. The ignition of fire-damp. By HUBERT FRANK COWARD and RICHARD VERNON WHEELER. London 1925. pp. 25. ill.

— Paper No. 9. The lag on ignition of firedamp. By C. A. NAYLOR and RICHARD VERNON WHEELER. London 1925. pp. 16. ill.

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NATIONAL ASSOCIATION OF MASTER BAKERS, CONFECTIONERS AND CATERERS. Reports on research at the National Bakery School (Borough Polytechnic Institute), London, conducted by CHARLES DORÉE and JOHN KIRKLAND. (From the *Nat. Assoc. Review*, 1925.)

NATIONAL PHYSICAL LABORATORY. *Metrology Department*. Verification of weights: testing of balances: determination of densities. 1925. pp. 28.

PERKIN, FREDERICK MOLLWO. Recent progress in the peat problem. Paper read before the British Association at Southampton on August 27th, 1925. London 1925. pp. 24. ill.

PUIG, P. IGNACIO. Teoría de las valencias positivas y negativas. Barcelona 1924. pp. 31. ill.

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RADIUM. Le vingt-cinquième anniversaire de la découverte du radium (1898-1923). [Paris n.d.] pp. 86.

RAU, MADYAR GOPAL. The constituents of some Indian essential oils. Part XVI. (From the *Indian Forest Records*, 1924, 11.)

RAU, MADYAR GOPAL and SIMONSEN, JOHN LIONEL. The constituents of some Indian essential oils. Part XVII. (From the *Indian Forest Records*, 1925, 11.)

# PROCEEDINGS

## OF THE

# CHEMICAL SOCIETY.

Ordinary Scientific Meeting, Thursday, November 5th, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., D.Sc., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
John Young Buchanan .....	June 21st, 1877.	Oct. 16th.
Harold James Cross .....	Feb. 15th, 1917.	Oct. 17th.
Francis Jones.....	Dec. 4th, 1873.	Oct. 22nd.
Charles Eddy Potter .....	Dec. 5th, 1912.	Sept. 13th.

The PRESIDENT announced that Professors C. S. Gibson, G. T. Morgan, J. F. Thorpe, and W. P. Wynne, have been appointed by the Council to represent the Society on the Bureau of Chemical Abstracts, and that Professors T. M. Lowry, J. W. McBain, and J. C. Phillip will represent the Society on the Editorial Board of the Journal of Physical Chemistry, together with Professor F. G. Donnan, appointed by the Faraday Society.

Certificates were read for the first time in favour of :

Harold Frederic Betts, B.Sc., 17, The Broadway, Broadstairs.  
Edward Britnell, B.Sc., 9, Osterley Avenue, Isleworth.  
Reginald John Bromfield, 141, Constantine Road, N.W. 3.  
Francis Hereward Burstall, B.Sc., 12, Adelaide Road, Teddington.  
Archer John William Butterfield, 163, Northumberland Park, N. 17.  
John William Corran, B.Sc., Ph.D., A.I.C., Research Laboratory, Carrow Works, Norwich.  
John Harold Cottier, 52, Aspen Grove, Lodge Lane, Liverpool.  
John Horsfall Dyde, 18, Dean Road, Scarborough.  
George Malcolm Dyson, B.A., B.Sc., Ph.D., 36, Hillsborough Road, E. Dulwich, S.E. 22.  
Alfred Eccles, B.Sc., 18, Cambrian Terrace, Holbeck, Leeds.  
George Albert Elliott, M.Sc., 263, Kennington Road, S.E. 11.  
Eric Bertram Evans, B.Sc., 2, Boxmoor Terrace, Southchurch, Southend.  
Elinor Katharine Ewbank, B.A., 22, Park Crescent, Oxford.

- Elizabeth Monica Openshaw Farrow, M.A., 37, Chalfont Road, Oxford.  
 Oliver Free, B.A., The Lodge, Mansfield College, Oxford.  
 William Marshall Freeman, 1, Temple Gardens, Temple, E.C. 4.  
 Eva Florence Gee, The Station, L.N.E.R., Howsham, Lincoln.  
 George Vincent Hall, B.Sc., 6, Borough Road, Bridlington.  
 William Rowan Hare, 220, Eastfield, Peterborough.  
 Walter Healey, 28, Gooder Lane, Brighouse.  
 Thomas Henderson, M.C., M.A., B.Sc., Guildford Grammar School, West Australia.  
 Syed Husain, M.Sc., 112, Gower Street, W.C. 1.  
 Gilbert Jessop, M.Sc., Ph.D., 453, Glossop Road, Sheffield.  
 Brian Charles Lavers Kemp, B.A., Wellington College, Berks.  
 Banarsi Das Laroia, B.A., B.Sc., 3, Oxford Road, Teddington.  
 John Joseph Lennon, M.Sc., 6, Bartlemas Road, Oxford.  
 Ivan Roy McHaffie, B.A., M.Sc., 37, King Henry's Road, N.W. 3.  
 Neil McLean, M.A., B.Sc., 127, Blenheim Place, Aberdeen.  
 Leslie George Manchester, B.Sc., 557, Green Lanes, Hornsey, N. 8.  
 William Alfred Nottage Markwell, 26, Huntsmoor Road, S.W. 18.  
 Charles Henry Lawrence Miller, 50, Rowden Road, Beckenham.  
 Horace Winston Palmer, B.Sc., 15, Hollingdean Terrace, Brighton.  
 Austin McDowell Patterson, Antioch College, Yellow Springs, Ohio, U.S.A.  
 Ernest Phillis, B.Sc., 22, Fairfield Terrace, Dewsbury Road, Leeds.  
 Jonathan Pollitt, B.A., 17, Caversham Avenue, Palmers Green, N. 13.  
 Charles Raymond Porter, M.Sc., A.I.C., 126, Linden Road, Bournville, Birmingham.  
 Evan Emrys Price, B.Sc., Rock House, Heathfield, Swansea.  
 Rose Rachel Sass, B.Sc., Newnham College, Cambridge.  
 Albert Seiver, B.Sc., A.I.C., 84, Vineyard Hill, Wimbledon Park, S.W. 19.  
 Frederick Francis Percival Smith, B.A., B.Sc., Peterhouse, Cambridge.  
 Robert Frederick Smith, 254, Higham Hill Road, Walthamstow, E. 17.  
 William Ernest Soper, B.Sc., 50, Aislibie Road, Lee, S.E. 12.  
 Herbert Kenneth Southern, B.Sc., Government Laboratory, Strand, W.C. 2.  
 Frank Harland Swire, 152, Queen's Road, Halifax.  
 Harold James Tattersall, B.Sc., Ph.D., 141, Thorold Road, Ilford.  
 Elvera Annie Tricker, 319, Norwich Road, Ipswich.  
 Norman Leopold Tyler, 9, St. Paul's Gardens, Spennymoor.  
 Herbert Ward Vernon, B.Sc. 245, Albert Road, N. 22.  
 Ewart Harrod Williams, B.Sc., A.I.C., 31, Thornsbeach Road, Catford, S.E. 6.  
 Gwyn Williams, B.Sc., Cae Ffynnon, Llandudno Junction.  
 John Laurence Wiltshire, B.Sc., 36, Fordel Road, Catford, S.E. 6.  
 Wilfred Fisher Wyatt, M.Sc., North Anston, Nr. Sheffield.

The following were formally admitted Fellows of the Chemical Society: W. J. V. Ward, H. F. Halliwell, R. J. W. Le Fèvre, I. J. Faulkner, J. Thurgood, and T. W. Jones.

The following papers were read:

- "Further studies on a new chlorinating agent. Preparation of polychloro-derivatives of toluene." By O. SILBERRAD.  
 "The configuration of the ammonium ion." By W. H. MILLS and E. H. WARREN.

The following paper was taken as read :

“ Ring-chain tautomerism. Part XV. The phenol-succineins and -glutareins.” By S. DUTT.

Ordinary Scientific Meeting, Thursday, November 19th, 1925 at 8 p.m., Professor W. P. WYNNE, D.Sc., F.R.S., Vice-President in the Chair.

The CHAIRMAN referred to the loss sustained by the Society, through death, of the following Fellows :

	Elected.	Died.
John Lloyd T. Jones .....	Feb. 7th, 1901.	Nov. 12th.
Frank George Pope .....	Feb. 18th, 1909.	Oct. 29th.
Robert Llewellyn Taylor .....	Jan. 15th, 1874.	Nov. 8th.

The CHAIRMAN announced that :

1. The Council has decided that the next Annual General Meeting and Dinner to take place on Thursday, March 25th, 1926, shall be held in Manchester. A local Sub-Committee has been appointed to make arrangements and full particulars will be announced later.

2. An Informal Meeting will be held in the Rooms of the Society on Thursday, December 17th, immediately after the conclusion of the formal business of the Ordinary Scientific Meeting at 8 p.m. Light refreshments will be provided, and smoking will be permitted, except on the Library Floor. The Council will welcome assistance from Fellows who can add to the interest of the Meeting by showing experiments or exhibiting apparatus, and those able to do so are requested to communicate with the Assistant Secretary not later than Monday, December 7th.

The following were formally admitted Fellows of the Chemical Society : Cyril C. Harris, John S. Carter, and T. H. Clare.

Certificates were read for the first time in favour of :

William Blakey, jun., B.A., 14, Marshall Road, Cambridge.

Herbert Clayton, M.A., B.Sc., The Dyson Perrins Laboratory, South Parks Road, Oxford.

John Charles Forsyth, 62, Worcester Street, Christchurch, New Zealand.

Ankarath Sankunni Mannadi Nayar, M.B., B.S., Ph.D., The Medical College, Madras.

William Bennett Price, B.Sc., The Laurels, Woolwich Road, Belvedere.

Madhavlal Sukhlal Shah, M.Sc., 22, Oxford Road, Putney, S.W. 15.

George Ernest Thompson, 7, Campbell Road, Bow, E. 3.

Bernard William Town, B.Sc., A.R.C.S., 79, The Grove, Hammersmith, W. 6.

Victor Martin Trikojus, B.Sc., Queen's College, Oxford.

Henry Woolf, P.O. Box 14, Broken Hill, Northern Rhodesia.

The following Certificate has been authorised by the Council for presentation to ballot under Bye-Law I (2) :

Edgar Calvin Le Roy Miller, M.D., Medical College of Virginia, Richmond Va., U.S.A.

The following papers were read :

- "The constitution of the metallic ozonides." By E. C. C. BALLY and R. W. RIDING.
- "Studies of dynamic isomerism. Part XX. Amphoteric solvents as catalysts for the mutarotation of the sugars." By T. M. LOWRY and I. J. FAULKNER.
- "Studies of valency. Part V. Absorption spectra of halogen and sulphonic derivatives of camphor. Origin of the ketonic absorption band." By T. M. LOWRY and G. OWEN.
- "Studies of valency. Part VI. General and selective absorption of halogen derivatives of methane. The origin of general absorption." By T. M. LOWRY and R. R. SASS.

The following paper was taken as read :

- "Studies of valency. Part VII. Surface polarity and the reaction of ethylene and chlorine. The effect of the adsorbed water layer." By R. G. W. NORRISH and G. G. JONES.

List of papers, or abstracts thereof, received between October 16th and November 19th, 1925. (This list does not include the titles of papers which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

- "Polymerisation of  $\beta$ -glucosan. The constitution of synthetic dextrans." By J. C. IRVINE and J. W. H. OLDHAM.
- "The action of mercurous nitrate on chloroauric acid." By W. B. POLLARD.
- "The freezing of inorganic hydrogels." By J. R. I. HEPBURN.
- "The bromination of some 5-substituted 1-phenylbenzthiazoles." By R. F. HUNTER.
- "Studies on the dependence of optical rotatory power on chemical constitution. Part VI. Rotatory powers of phenyl, *o*-, *m*-, *p*-tolyl and  $\beta$ -naphthyl derivatives of *d*-camphorimide and *d*-camphoramidic acid." By B. K. SINGH and A. N. PURI.
- "Transformations of the sugar nitrates." By J. W. H. OLDHAM.
- "Studies in colour and constitution. Part I. The positional bathochromic influence of the methylthiol group, alone, and in conjunction with the methoxy-group." By H. H. HODGSON and F. W. HANDLEY.

- "The photochemical oxidation of hydriodic acid in ultra-violet light. Part I." By T. MOORE.
- "Ring-chain tautomerism. Part XVII. Instances showing how glutaric derivatives can simulate succinic compounds." By S. DUTT.
- "A theory of colour on the basis of molecular strain. The effect of chromophoric superposition." By S. DUTT.
- "The influence of the intensity of illumination on the velocity of photochemical changes." By F. BRIERS, D. L. CHAPMAN, and E. WALTERS.
- "The salting-out effect. The influence of electrolytes on the solubility of iodine in water." J. S. CARTER.
- "Germanium. Part II. Germanium tetrachloride and its ammonia compounds." By W. PUGH and J. S. THOMAS.
- "The action of alcoholic soda and potash upon chloronitrobenzene." By D. H. RICHARDSON.
- "The partial pressures of aqueous ethyl alcohol." By H. J. E. DOBSON.
- "A comparison of some of the physical properties of the alkali cyanates and azides." By J. A. CRANSTON and A. Y. LIVINGSTONE.
- "Reactions for nitrites." By B. C. McEWEN.
- "Lead dihydride and lead tetrahydride." By E. J. WEEKS.
- "Some reactions of organic thiosulphates." By H. B. FOOTNER and S. SMILES.
- "Air oxidation of titanous and vanadous sulphates." By A. S. RUSSELL.
- "Complex formation in lead nitrate solutions. Part II. The quaternary system potassium nitrate-lead nitrate-barium nitrate-water." By S. GLASSTONE and E. J. RIGGS.
- "Polymerisation of acetone by calcium carbide." By T. HOPKINS.
- "Action of zinc alkyl halides on nitric esters." By T. HOPKINS.
- "Observations on the Claisen reaction." By G. T. MORGAN and E. HOLMES.
- "The specific heats of hydrocyanic acid. A reply." By E. H. INGOLD.
- "The relation of homogeneous to catalysed reactions. The catalytic decomposition of hydrogen iodide on the surface of platinum." By C. N. HINSHELWOOD and R. E. BURK.
- "The action of hydrogen fluoride on compounds of selenium and tellurium. Part II. Tellurium dioxide." By E. B. R. PRIDEAUX and J. O'N. MILLOTT.
- "Halogenation of 2:6-dimethylbenzbisthiazole and of 2:4-diphenyl-3:5-diphenyliminotetrahydro-1:2:4-thiodiazole." By R. F. HUNTER.

- "The reaction between hydroxylamine and ferric chloride." By A. D. MITCHELL.
- "The equilibria underlying the soap-boiling processes. The system potassium oleate-potassium chloride-water." By J. W. MCBAIN and W. J. ELFORD.
- "The solubility of sodium iodide in ethyl alcohol." By F. E. KING and J. R. PARTINGTON.
- "Iodination in the carbazole series." By S. H. TUCKER.
- "The chemistry of the caryophyllene series. Part I." G. G. HENDERSON, J. M. ROBERTSON, and (in part) C. A. KERR.
- "On the Budde effect in bromine. Part I. The photoactive constituent in wet bromine." By B. LEWIS and E. K. RIDEAL.
- "On the Budde effect in bromine. Part II. The kinetics of the reaction and the light absorption of wet and dry bromine." By B. LEWIS and E. K. RIDEAL.
- "The constitution of the benzene nucleus." By B. C. McEWEN.
- "Keto-enol isomerism of ethylenebisacetylacetone." By G. T. MORGAN and C. J. A. TAYLOR.
- "A buffer mixture for the alkaline range of hydrogen-ion concentration determinations." By W. R. G. ATKINS and C. F. A. PANTIN.
- "The influence of carbon rings on the velocity of reactions involving their side-chains. Part I. The hydrolysis of cyclic and open-chain malonic esters." By R. GANE and C. K. INGOLD.
- "The condensations of 3-bromo-, and 3-nitro-*p*-dimethylamino-benzaldehydes with ethyl acetoacetate and ammonia." By L. E. HINKEL and W. R. MADEL.
- "The replacement of calcium carbonate by iron pyrites in nature." By C. O. HARVEY.
- "A revision of the structural formula of glucose." By W. CHARLTON, W. N. HAWORTH, and S. PEAT.

**CERTIFICATES OF CANDIDATES FOR ELECTION AT  
THE BALLOT TO BE HELD AT THE ORDINARY  
SCIENTIFIC MEETING ON THURSDAY, DECEMBER 3RD,  
1925.**

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ANDREW, ROBERT LESLIE, Dominion Laboratory, Wellington, New Zealand. British (by birth). Analyst. Nineteen years' experience in Dominion Laboratory, N.Z., now senior assistant in charge of Food and Drugs work. Published work: "The Colorimetric Estimation of Lead in Cream of Tartar," *Analyst*, 1924, p. 129. "The Cryoscopic Method for the Detection of Added Water in Milk" (appendix to 50th Annual Report, Dominion Laboratory). (Signed by) J. S. MacLaurin, P. W. Robertson, K. M. Griffin.

BAISSAC, LOUIS, Curepipe Road, Mauritius (Indian Ocean). British. Sugar Technologist, Department of Agriculture, Réduit, Mauritius. Lecturer



in Sugar Technology, College of Agriculture, Réduit, Mauritius. (*Signed by*) James P. Ogilvie, H. Tempany, W. H. Edwards.

BARKER, WILLIAM FRANCIS, Rhodes University College, Grahamstown, S. Africa. Professor of Chemistry. Ph.D. (Liverpool). (*Signed by*) I. M. Heilbron, E. C. C. Baly, R. A. Morton.

BASDEN, RALPH, 11, Ada St., Hamilton, Newcastle, N.S.W. Teacher of Chemistry. I have been engaged for four years as Teacher of Science at Sydney Grammar School; two years Teacher of Organic and Physical Chemistry at Newcastle Technical College, and four years in Manufacturing and Analytical Chemistry. (*Signed by*) A. R. Penfold, Robt. Grant, Fred J. Berry, Richard W. Challinor.

BELL, FRANK, 11, Edwy Parade, Gloucester. British. Student. Research student at Battersea Polytechnic. (*Signed by*) J. Kenyon, F. C. Ray, Henry Phillips, A. Houssa, Harold Hunter, P. W. B. Harrison, S. Greenberg.

BENNETT, ARTHUR NEVILLE COPNALL, 27, Dale Rd., Luton. British. Research Chemist to B. Laporte, Ltd., Luton. B.Sc. (Hons.) London. Have done research under Prof. Donnan at University College, and hope to publish shortly. (*Signed by*) W. E. Garner, D. McKie, Thomas Iredale.

BETTS, HAROLD FREDERICK, 17, The Broadway, Broadstairs, Kent. British. Research Student, East London College (Univ. of London). B.Sc. (Lond.), 2nd Class Hons. Chemistry. (*Signed by*) J. R. Partington, D. C. Jones, E. E. Turner.

BIRD, JOHN CECIL, 72, Dyne Rd., Kilburn, London, N.W. 6. British. Research and Works Chemist. B.Sc. (London), A.I.C., Associate of Univ. College of Nottingham. Science Master, Grammar School, Daventry. Chemist to Messrs. L. B. Holliday & Co., Ltd., Huddersfield. Chief Chemist and Works Manager to J. W. Drysdale & Co., London. Chemist to Messrs. Intermediates and Explosives, Ltd. (Bolckow, Vaughan & Co.), Co. Durham. Chemist to Messrs. Crookes Laboratories (British Colloids, Ltd., London). Investigation with Prof. H. H. Hodgson, M.A., into Absorption Spectra of Standard Dyestuffs (Huddersfield). (*Signed by*) Herbert Henry Hodgson, F. S. Kipping, E. R. Trotman.

BIRKETT, LIONEL CHRISTOPHER WILLIAM, Moor House, North Rd., Spennymoor, Co. Durham. British. Analytical Chemist on Coke Oven and By-products Plant. 5½ years' experience in Ironworks and Coke Oven laboratories. B.Sc. (3rd Class Hons.) after 3 years' study at Armstrong College, Newcastle-on-Tyne. (*Signed by*) W. N. Haworth, G. C. Leitch, H. V. A. Briscoe.

BOYD, JAMES, P.O. Box 1162, Johannesburg, S. Africa. British. Chief Examiner of Mine Air, Chamber of Mines, Johannesburg (and Assistant to General Manager, Chamber of Mines). F.I.C., A.R.T.C. (Glasgow). Assistant to Professor of Chemistry, Royal Technical College, Glasgow, 1908-11. Chemist, Goldfields Lab., Transvaal, 1912-13. Chief Examiner of Mine Air, Chamber of Mines, Johannesburg, 1914 to date. Author of various reports on Dust in Mine Air and Methods of investigating same (published in "Chamber of Mines Annual Reports," and for circulation to the mines of the Rand). Student, Royal Technical College, Glasgow, 1904-08. (*Signed by*) G. G. Henderson, Thomas Gray, F. J. Wilson.

BRADHURST, FRANK SYMONDS, Bondi, Sydney, and c/o Holbrooks Ltd., Danks St., Waterloo, Sydney. Chief Chemist and Factory Manager. Matriculated from Sydney High School at Leaving Certificate Examination; obtained Scholarship available at the Sydney Technical College. Here I obtained the Honours Diploma with College Medal for year in Organic Chemistry, thereby becoming an Associate of the Sydney Technical College (A.S.T.C. Chem.).

Associate of the Australian Chemical Institute (A.A.C.I.). Chemist at Stedman-Hendersons, Ltd., Sweet Manufacturers, for  $2\frac{1}{2}$  years, then at Holbrooks (Australasia), Ltd., of Sydney, for 3 years, where I now hold the above position. I desire admission to the Chemical Society in order to keep in touch with modern research in the field of Food Analysis, and Food Manufacture. (*Signed by*) Richard W. Challinor, Fred J. Berry, Robert Grant, Arthur R. Penfold, S. E. Sibley.

BRITNELL, EDWARD, 9, Osterley Av., Isleworth, Middlesex. English. Chemist. B.Sc. (Honours Chemistry), London, July 1925. Assistant for 3 years to G. N. Huntly, 325, Kennington Rd., S.E. Assistant for  $1\frac{1}{2}$  years to G. T. Holloway & Co., 13, Emmett St., Limehouse. (*Signed by*) William G. Wagner, G. Nevill Huntly, Herbert F. Stephenson.

BROMFIELD, REGINALD JOHN, 141, Constantine Rd., Hampstead, N.W. 3. English. Assistant to Biochemist, The Hospital for Sick Children, Great Ormond St., W.C. For three years laboratory assistant at University College, London, under Prof. F. G. Donnan and Prof. N. Collie. For one year Acting Biochemist to Children's Hospital, Gt. Ormond St. For past two years Biochemical assistant, Hospital for Sick Children, Great Ormond St. Desire to become a member in order to receive the Journal and to keep in touch with current chemical literature, together with access to Library. (*Signed by*) J. N. Collie, Henry Terrey, Fred J. Kettel, J. Wielife Peck.

BURSTALL, FRANCIS HEReward, 12, Adelaide Road, Teddington, Middlesex. British. Research Chemist. D.S.I.R. Chemical Research Laboratory, Teddington. 1st Class Honours B.Sc., Birmingham University. (*Signed by*) G. T. Morgan, E. Holmes, C. E. Wood.

BUTTERFIELD, ARCHER JOHN WILLIAM, 163, Northumberland Park, Tottenham, N. 17. English. Articled Pupil in Engineering. Is desirous of keeping in touch with progress in the Science of Chemistry by attending the meetings and receiving the publications of the Society. (*Signed by*) W. J. A. Butterfield, Ernest M. Hawkins, E. R. Bolton.

CARLILE, JOHN HILDRED GEORGE, 29, Orlando Rd., Clapham, S.W. 4. British. Chemical Research Student, Royal College of Science. A.R.C.Sc., B.Sc. (*Signed by*) H. J. T. Ellingham, James C. Philip, H. F. Harwood.

CHALK, LESLIE JAMES, 14, Shrubbery Rd., Southall, Middx. Student (East London College). B.Sc., 1st Class Hons. in Chemistry. J. R. Partington, E. E. Turner, Elwyn Roberts.

CHARAN, RAMA, Allahabad, India. Indian (British). Glass Technologist, Govt. of India State Technical Scholar, B.Sc. from Allahabad University, 1922. Subjects: Maths., Physics, Chemistry, and English. B.Sc. Tech. from Sheffield University, 1924. Subjects: Glass Technology, Fuel, Refractory Materials, Geology and Mineralogy of Glassmaking Materials. For one year after graduation did research work on glasses containing more than one alkaline oxide and silica-lime. (*Signed by*) W. E. S. Turner, C. J. Peddle, F. G. Tryhorn.

CORRAN, JOHN WILLIAM, Research Laboratory, Carrow Works, Norwich. British. Physical and Biochemist. B.Sc. (Liv.), 1st Class Hons. Chem., 1921; Ph.D. (Liv.), 1923; A.I.C. Two years Research Physical Chemistry under Prof. W. C. M. Lewis; two years as physical and biochemist to Liverpool Cancer Research Committee. Publications: *J. Amer. Chem. Soc.*, 1922, 44, 1673; 1923, 45, 1627. *Biochem. J.*, 1924, 18, 1358, 1364. (*Signed by*) W. C. M. Lewis, E. C. C. Baly, E. Morrison, Leslie J. Harris.

COTTER, JOHN HAROLD, 52, Aspen Grove, Lodge Lane, Liverpool. British. Certificated School-teacher; formerly a student of Sheffield University. I

wish to obtain the Fellowship of the Society in order to receive the Journal and Abstracts, and thus keep in touch with advances in Chemistry. (*Signed by*) W. P. Wynne, F. G. Tryhorn, E. G. Turner, D. M. Bennett.

CROWTHER, EDWARD MORTIMER, Rothamsted Exptl. Station, and Bourtree, 24, Clarence Road, Harpenden, Herts. British. Assistant Physical Chemist and "Empire Cotton Growing Corporation," Soil Physicist, Rothamsted Exptl. Station. D.Sc. (Leeds), F.I.C., A.Inst.P. Publications on Physical Chemistry of Soils. *Journ. Agric. Sci.*, 1925, **15**, 201-255, 300-302, 303-306; *Trans. Faraday Soc.*, 1922, **17**, 317-321. Conjointly: *Journ. Agric. Sci.*, 1924, **14**, 221-231; 1925, **15**, 68-88; *Proc. Royal Soc.*, 1925, **106A**, 33-51, 215-222, 233-242; *Annals of Applied Biology*, 1925, **12**, 152-190. (*Signed by*) E. J. Russell, H. J. Page, C. T. Gimingham.

DICKINSON, FRANK EDWIN, Research Establishment, Sutton Oak, St. Helens, Lancs. British. A/g Superintendent, The Research Establishment, Sutton Oak, St. Helens, Lancs. Actively engaged in Chemical Industry as Analytical and Research Chemist and as Assistant Manager and Manager of Chemical Works for past fourteen years. Educated at King Edward's School, Stratford-on-Avon, and University of Birmingham. No papers published as all work of secret nature or commercial value. (*Signed by*) J. Davidson Pratt, E. Wheeler, Francis H. Carr.

DOLPHIN, JOSEPH RAYMOND, Chemical Department, University Rd., Edgbaston, Birmingham. British. Research Student. Pass B.Sc. Birmingham, 1st Class, 1923; Honours B.Sc. Birmingham, 1st Class, 1924. Research Student under Professor Morgan, O.B.E., D.Sc., F.R.S., from 1924-25 to become Research Chemist at J. A. Crabtree & Co., Ltd., Walsall, in Sept. 1925. (*Signed by*) G. T. Morgan, C. E. Wood, E. Ashley Cooper.

DONOVAN, WILLIAM, Dominion Laboratory, Wellington, New Zealand. British. Analyst, Dominion Laboratory, N.Z. M.Sc. (New Zealand University). Twenty years' experience in analytical work; now Assistant Dominion Analyst. Published work includes "Corrosion of Muntz Metal in Sea Water," *J.S.C.I.*, XLIII, 13, 72x; "Estimation of Nitrogen in Coal," *The Analyst*, Feb. 1924. (*Signed by*) J. S. MacLaurin, P. W. Robertson, K. M. Griffin.

DUNN, JOHN STANLEY, 39, Victoria Park, Cambridge. British. Chemist. M.A. (Cantab.), Ph.D. (London), A.I.C. Late Research Chemist, Calico Printers Assocn., Manchester; now Research Chemist, British Non-Ferrous Metals Res. Assocn. With Dr. E. K. Rideal: *T.*, 1923, 123, 1242; *T.*, 1924, 125, 676. (*Signed by*) R. G. W. Norrish, Eric K. Rideal, H. McCombie.

DYDE, JOHN HORSEFALL, 18, Dean Rd., Scarborough. British. Student at the University, Leeds, who intends to pursue post-graduate work in Biochemistry. Final year B.Sc. (Honours Chemistry). (*Signed by*) C. K. Ingold, B. Topley, H. M. Dawson.

DYSON, GEORGE MALCOLM, 36, Hillsborough Road, E. Dulwich, London, S.E. 22. British. Research Chemist. B.A. (Oxon.), B.Sc., Ph.D. (London). Research in Organic Chemistry, including work on the Reactions of Thiocarbonyl Chloride with Amino-compounds, Phenols, etc. *J.C.S.*, Trans., Sept., 1924, 125, 1702; "The Reactions of Thiocarbonyl Chloride. Pt. I." (*Signed by*) D. L. Chapman, H. J. George, L. Rubenstein.

ECCLLES, ALFRED, 18, Cambrian Terrace, Holbeck, Leeds. British. Research Student (University of Leeds). B.Sc., 1st Class Hons. (Pure Chemistry), 1925. (*Signed by*) C. K. Ingold, P. K. Dutt, W. A. Wightman, J. W. Baker.

EDWARDS, EDWIN FRANCIS, Kogarah, Sydney, N.S.W., c/o Holbrooks (Australasia), Limited, Waterloo, Sydney. Works Chemist and Assistant

Factory Manager. Matriculated from High School at Leaving Certificate Examination, and gained Scholarship to Sydney Technical College. Attended the above College for five years—thereby completing the Diploma Course—and was subsequently granted the Associateship of the College, and the Diploma in Organic Chemistry. I am also an Associate of the Australian Chemical Institute. I was Assistant Chemist at the Woolwich Chemical Co., Sydney, for a period of two years, and Analyst at H.M. Customs, Sydney, for twelve months. At present I hold the above-mentioned position on the Staff of Holbrooks (Australasia), Limited, of Sydney. I desire admission to the Chemical Society in order to keep in touch with modern chemical literature and progress. (*Signed by*) Richard W. Challinor, Fred J. Berry, Robert Grant, Arthur R. Penfold, S. E. Sibley.

EDWARDS, JOHN MOELWYN, 92, Jamaica Rd., Rotherhithe, S.E. 16. British. Chemist and Pharmacist and Optician. (1) Early education at the Meirioneth County Grammar School. (2) Three years student of Chemistry at the Festiniog Higher Grade School. (3) Studied Analytical Chemistry and Physics under Mr. J. Thomas, B.Sc., at Muter's School of Chemistry. (4) Passed the Qualifying Examination of the Pharmaceutical Society of Great Britain in 1905. (5) Four years Sight Testing Optician with Mr. Hugh Jones, F.S.M.C., D.B.O.A. Am particularly anxious to keep in touch with Analytical work. (*Signed by*) Frank B. Arnold, John J. Laws, Percy Barrs.

ELLIOTT, GEORGE ALBERT, 263, Kennington Road, London, S.E. 11. British. Ramsay Memorial Fellow. M.Sc. (Lond.). (*Signed by*) L. F. Gilbert, S. Barratt, W. E. Garner.

EVANS, ERIC BERTRAM, 2, Boxmoor Terrace, Southchurch, Southend, Essex. English. Student. For two years a student at East London College; at present engaged in research there. Awarded 2nd Class in B.Sc. Hons. Lond., 1925. (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

EWBANK, (Miss) ELINOR KATHARINE, 22, Park Crescent, Oxford. British. Engaged in original research. Took 1st Class in Honours, School of Chemistry, Oxford, 1903. E. C. C. Baly and E. K. E., 87, 1347; 87, 1355. N. V. Sidgwick and E. K. E., 119, 486; 121, 1844; 125, 2268. (*Signed by*) W. H. Perkin, N. V. Sidgwick, D. Ll. Hammick.

FARROW, (Miss) ELIZABETH MONICA OPENSHAW, 37, Chalfont Rd., Oxford. British. Demonstrator in Old Chemistry Dept., Oxford. Lecturer in Chemistry to 5 Women's Societies. M.A. (Oxon.) (*Signed by*) W. H. Perkin, N. V. Sidgwick, B. Lambert, M. P. Applebey, Allan F. Walden, E. G. J. Hartley, Frederick Soddy, J. Masson Gulland, S. G. P. Plant.

FREE, OLIVER, The Lodge, Mansfield College, Oxford. British. Demonstrator of Inorganic Chemistry. B.A., 2nd Class Honours. Research Student in Physical Chemistry (Radioactivity). (*Signed by*) M. P. Applebey, Frederick Soddy, B. Lambert, N. V. Sidgwick, A. F. Walden.

FREEMAN, WILLIAM MARSHALL, 16, Oakwood Avenue, Beckenham, Kent. British. Of the Honourable Society of the Middle Temple, Barrister-at-Law, Recorder of Stamford, and formerly Member of the Pharmaceutical Society of Gt. Britain. Author of "The Patents and Designs Act 1907, with Appendix on Chemical Patents." Occasional contributor to legal and other journals on Food and Drugs legislation, etc. Interested particularly in the promotion of the study of chemico-legal science especially with reference to the administration of the criminal law. (*Signed by*) Ernest C. Bennison, H. Berry, Harry Silvester.

GEE, EVA FLORENCE, The Station, L.N.E.R., Howsham, Lincoln. British.

Student of Chemistry at Bedford College. (*Signed by*) J. F. Spencer, H. Crompton, J. Stewart.

GEMMELL, JAMES WALTER SHANKS, Helen's Villa, Fleming Place, St. Andrews. British. Research Chemist. B.Sc. (Hons.) St. Andrews; now employed in Research Dept., Jute Industries, Ltd., Dundee, and desirous of keeping in touch with recent developments in chemical science. (*Signed by*) A. Killen Macbeth, James Craik, John Pryde.

GLOVER, FRANCIS REGINALD, 98/100, St. Peter's Street, Nottingham. British. Managing Director, Cooke & Glover, Engineers, Ltd., Engineers and Consulting Chemists, Nottingham, M.I.H.V.E., A.M.I.S.E. (*Signed by*) E. B. R. Prideaux, J. B. Firth, B. D. Shaw.

GOUDIELOCK, WILLIAM BOUCH O'BRIEN, 28, Fairfield Lane, Barrow-in-Furness. British. Chief Analyst, Vickers Ltd., Barrow-in-Furness. Full Technological Certificate, City and Guilds Institute, in Chemistry, Metallurgy, and Iron and Steel. Pupil in Vickers' Lab. under H. B. Weeks, F.I.C., for 5 years. Chief Laboratory Assistant for 8 years. Chief Analyst ever since. Lecturer for 2 years to Vickers' Engineering Apprentices on Chemical and Metallurgical Subjects in Connection with Firm's Scheme for Higher Education of Apprentices. Lecturer to Barrow Engineer's Assoc., Jan. 1920 and Jan. 1923. I am desirous of keeping in close touch with modern developments in Scientific Chemistry. (*Signed by*) H. B. Weeks, A. H. Munday, W. J. Davison.

GRIGG, FELIX JOHN THEODORE, Christchurch (N.Z.). British. Government Analyst, Government Buildings, Christchurch, N.Z. M.Sc. (N.Z.) with Honours in Chemistry. A.I.C. (Great Britain). Seven years' experience in analytical work. Now Government Analyst at Christchurch (N.Z.). Published work: "Geochemistry of the Thermal Lakes, North Island, N.Z." (*N.Z. Journal of Science and Technology*, 1922, Volume 5, page 156). (*Signed by*) J. S. Maclaurin, P. W. Robertson, K. M. Griffin.

HALL, GEORGE VINCENT, 6, Borough Road, Bridlington, Yorks. British. Student. Bachelor of Science, University of Leeds, June 1925. (*Signed by*) C. K. Ingold, H. M. Dawson, W. Lowson, P. K. Dutt.

HALL, JOHN, 202, Burton Rd., Derby. British. Chemist. M.Sc. (Leeds), A.I.C. Three years in Lab. of Sir W. G. Armstrong-Whitworth & Co.; two years in Lab. Dyehouse and Colour Plant of British Celanese. *J.C.S.*, 123, 2029-2037. (*Signed by*) A. G. Perkin, G. Reeves, W. P. Skertchly.

HARE, WILLIAM ROWAN, 220, Eastfield, Peterborough. British. Student of Chemistry in the University of Oxford. Desirous of receiving literature (*Signed by*) D. Ll. Hammick, S. G. P. Plant, E. Hope.

HEALEY, WALTER, 28, Gooder Lane, Brighouse. English. Student, University of Leeds. Chemical Student who hopes to take up research. (*Signed by*) C. K. Ingold, P. K. Dutt, W. A. Wightman.

HENDERSON, THOMAS, M.C., M.A., B.Sc., Toronhill Schoolhouse, Dunfermline. Scottish. Demonstrator in Chemistry (Inorganic), University of Leeds. M.A., B.Sc., St. Andrews, 1921. Holding a grant from the Dept. of Scientific and Industrial Research, carried on research work at St. Andrews University, under direction of Sir James C. Irvine, and have held the appointment noted above since October 1922. Vol. 121, 1922, Trans., p. 892; Vol. 123, 1923, Trans., p. 1130. (*Signed by*) R. Whytlaw-Gray, H. S. Patterson, B. Topley, W. Lowson, J. C. Irvine, Ettie S. Steele.

HIRST, HERBERT SM, Trinity College, Cambridge. British. Research Assistant to Dr. E. K. Rideal, under Department of Scientific and Industrial Research Regulations. First class honours graduate in Physics and Chemistry

of St. Andrews University, with two years' research experience in Cambridge. "The Thermal Decomposition of Nitrogen Pentoxide," 1925, 127, 657. (*Signed by*) Eric K. Rideal, W. H. Mills, Ulick R. Evans.

HUSAIN, SYED, 112, Gower St., London, W.C.1. Indian. Student. M.Sc. (Aligarh Muslim University, India). (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

IWADARE, TORU, c/o Banyu Pharmaceutical Co., Ltd., 174, Shimomeguro, Tokyo, Japan. Japanese Proper. Became Chief Chemist and Managing Director of Banyu Pharmaceutical Co., Ltd., in September 1915. Have two years' experience as Assistant of the Chemical Dept. of the Tokyo Imperial University, and ten years' experience as Chief Chemist and Managing Director of Banyu Pharmaceutical Co., Ltd. Graduate, College of Science (Chemistry), Tokyo Imperial University, 1913. (*Signed by*) Joji Sakurai, T. Takamatsu, Y. Asahina.

JAYEWARDENE, DAVID CHRISTOPHER MENDIS, Fern Bank, Moratuwa, Ceylon. Sinhalese, British. Science Master, Prince of Wales' College, Moratuwa. (1) Science Master, St. John's College, Panadura, Ceylon (1918 and 1919). (2) Asst. Chemist, Butter Substitutes Supplies, Ltd., Colombo (1920). (3) Science Master, Prince of Wales' College, Moratuwa (since 1921). (*Signed by*) W. N. Rae, J. P. C. Chandrasena, K. V. Rau.

JESSOP, GILBERT, 453, Glossop Rd., Sheffield. British. Research Chemist. M.Sc., Ph.D. (Sheffield). Three years' Research in Physical Chemistry. Papers in the *Proc. Roy. Soc.*, 1925, 98B, 206 (with Mr. N. K. Adam), and in the *J.C.S.* (with Mr. F. G. Tryhorn), 1925, 127, 1320; (with Mr. N. K. Adam), 1925, 127, 1863. (*Signed by*) W. P. Wynne, F. G. Tryhorn, N. K. Adam.

JOHNSON, CHARLES BENJAMIN, 134, Preston New Road, Blackburn. British. Minister of Religion (Fellow of Royal Astronomical Society). I desire to keep abreast, by means of the Society's Publications, of advance in General and Physical Chemistry. (*Signed by*) G. W. F. Holroyd, J. Hindle, Robert H. Pickard.

JONES, WALTER IDRIS, 7, Manor Street, Cambridge. Welsh. Research Student. Gonville and Caius College, Cambridge. Ph.D. (Cantab.), B.Sc. (Wales), etc. *Trans. Chem. Soc.*, 1923, 123, 2688; 1924, 125, 2590. (*Signed by*) Hamilton McCombie, John Dexter, Harold A. Scarborough.

KEENAN, HENRY WILFRID, 80, Upper Richmond Road, East Sheen, S.W. 14. British. Works Chemist. Practical experience in various branches of Analytical and Manufacturing Chemistry founded on a three years' Systematic Apprenticeship (with evening studies) under Dr. Julius Holzapfel and Dr. P. E. Bowles, F.I.C., by whom indentures are signed. Invented processes (including design and erection of plant for large scale production) dealing with (a) Paint and Varnish Industry, (b) Celluloid Industry, (c) Oils, and operated successfully. (*Signed by*) Charles Dorée, Francis Arnall, J. C. Crocker.

KEMP, BRIAN CHARLES LAYERS, Wellington College, Berks. British. Schoolmaster. Chemistry Master (VIth Form) at Wellington College; B.A. (Oxon.). 1922-23, research work on derivatives of Dianisoyl Methane. (*Signed by*) G. Watson Gray, D. LL. Hammick, B. Lambert.

KING, CHARLES, F.S.A. (Scot.), 21, Newton Place, Glasgow. British. Electro-therapeutist. Fellow of the Society of Science, Lond. Applicant is in practice as Electro-therapeutist, and is desirous of keeping in touch with current chemical progress. (*Signed by*) G. G. Henderson, J. Roberts, Archd. N. Currie.

KOCH, FREDERICK KARL VICTOR, 9, Crossfield Road, Hampstead, N.W. 3.

English. Research in Physical Chemistry, Imperial College of Science and Technology. B.Sc. (1st Class), A.R.C.S. (2nd Class). (*Signed by*) James C. Philip, H. J. T. Ellingham, H. F. Harwood.

LANGFORD, CHARLES DUDLEY, 43, Ashbourne Av., Temple Fortune, London, N.W. 11. British. Research Student (Organic Chemistry), Royal College of Science. A.R.C.S., B.Sc. Honours (passed 1925, to be awarded 1926 owing to regulations). (*Signed by*) G. A. R. Kon, R. W. West, E. H. Farmer.

LAROLA, BANARSI DAS, Pindi Street, Ludhiana, Punjab, India. Indian. Student. B.Sc. (Hons.) Punjab University (India), B.A. (Hons.) Oxford University. At present student of Imperial College of Science and Technology (for Ph.D.). (*Signed by*) E. H. Farmer, G. A. R. Kon, M. A. Whiteley.

LASZLO, HENRY GUINNESS DE, 3, Fitzjohn's Avenue, Hampstead, N.W. 3. British. Research Chemist. B.A. Hons. (Cantab.), Ph.D. (Zurich). (*Signed by*) M. A. Whiteley, G. Ingle Finch, Samuel Smiles.

LEATHERBARROW, BERTRAM GREY, Hill Crest, Station Rd., Brimington, Chesterfield. British. Senior Assistant Teacher, Brimington Central School. Intermediate B.Sc. Two years subsequent graduation courses. Headmaster, Brimington Central Evening School, teaching all the Technical Courses. Student, Liverpool University 1919-1923. (*Signed by*) E. C. C. Baly, W. C. McC. Lewis, I. M. Heilbron, H. J. Stern.

LENHER, SAM, 15, Gordon Street, London, W.C. 1. American. Research Student at the Ramsay Laboratory, University College, London. Graduate of the University of Wisconsin (B.A. Degree), 1924. Internal student for the Ph.D. degree, University College, London, one year. McHaffie and Lenher, *J.C.S.*, 1925, 127, 1559-1572. (*Signed by*) F. G. Donnan, W. E. Garner, J. A. Currie.

LENNON, JOHN JOSEPH, 6, Bartlemas Road, Oxford. Irish. Research Student. M.Sc., National University of Ireland, 1924, 1851 Scholar. Paper in collaboration with Hugh Ryan, D.Sc., *Proc. Royal Irish Acad.*, xxxvii, B, p. 27. (*Signed by*) W. H. Perkin, Francis Lions, R. D. Haworth, John Rankin.

MACARTNEY, WILLIAM, c/o Grattan & Co., Ltd., Belfast. British. Pharmaceutical Chemist. Chief Chemist of Messrs. Grattan & Co., Ltd., Wholesale Manufacturing Chemists and Aerated Water Manufacturers. Member of the Pharmaceutical Society of Ireland. Vice-President North Irish Pharmaceutical Society, Vice-President Ulster Drug Trade Association. No published papers in the *Journal of the Chemical Society*. In order to keep in touch with current advances in Chemistry. (*Signed by*) Henry Wren, Chas. J. Still, A. W. Stewart, Theo. Harper.

McHAFFIE, IVAN ROY, 37, King Henry's Rd., London, N.W. 3. Canadian. Research Student, University College, London. B.A., M.Sc. University of Manitoba, Canada. "The Adsorption of Water from the Gas Phase on Plane Surfaces of Glass and Platinum," *J.C.S.*, 1925, 127, 1559-1572. (*Signed by*) F. G. Donnan, W. E. Garner, S. Barratt.

McLEAN, NEIL, M.A., B.Sc., 127, Blenheim Place, Aberdeen. British. Station Director of the British Broadcasting Station at Aberdeen. Applicant is a Master of Arts and Bachelor of Science of Glasgow University, and is much interested in chemical science and desirous of having the best available literature on this subject for the purposes of his work. (*Signed by*) J. F. Tocher, G. G. Henderson, Archd. N. Currie.

MANCHESTER, LESLIE GEORGE, 557, Green Lanes, Hornsey, N. 8. British. Student. Two years a student at East London College; now engaged in

research work at same college; awarded 2nd Class in B.Sc. Hons. Lond. 1925. (*Signed by*) J. R. Partington, E. E. Turner, R. J. W. Le Fèvre.

MARKWELL, WILLIAM ALFRED NOTTAGE, 26, Huntsmoor Road, S.W. 18. English. Chemist. Desire to receive the *Journal* and to keep in touch with the progress of Chemical Science. (*Signed by*) E. W. Lucas, S. Greenberg, F. C. Ray, J. L. White, Henry Phillips.

MARTIN, WILLIAM FRANCIS, 27, Shandon Crescent, Edinburgh. British. Work's Chemist, in the employment of Messrs. T. & H. Smith, Ltd., Blandfield Chemical Works, Edinburgh. Fellow of Institute of Chemistry (F.I.C.), Member of Pharmaceutical Soc. of Gt. Britain (M.P.S.). (*Signed by*) James Walker, Alexander J. Dey, James Watt.

MILLER, CHARLES HENRY LAWRENCE, 50, Rowden Rd., Beckenham, Kent. British. Student (B.Sc. Honours Chemistry) at East London College. At present doing research work. Desirous of keeping in touch with modern Chemical Research. (*Signed by*) J. R. Partington, E. E. Turner, D. C. Jones, W. H. Patterson.

MOORE, ARTHUR, Highfield, Oakworth, Keighley, Yorks. British. Student (Chemistry). 3rd Year (final) Hons. Chemistry, Royal Coll. of Science, London, S.W. 7. (*Signed by*) H. L. Riley, H. F. Harwood, H. D. Murray.

MORRISON, ALEXANDER JOHN, Sydney, N.S.W. Assistant Superintendent of Testing and Inspection, Public Works Dept., Sydney. *Training*: Student for 3 years (night course) in the Chemical and Assay Laboratory of the late William Grosse, Mining Engineer and Metallurgist. *Sydney Technical College*: 4 years' course practical chemistry; 3 years' course theoretical chemistry; 2 years' course organic chemistry. Engaged on special investigation in connection with fixed oils and alloys. *Original Papers*: (With F. R. Morrison), "Examination of the fixed oil of the Queensland Nut," read before the Sydney Technical College Chemical Society (Vol. 1, pages 84—88). "Testing of Sand for Use in Portland Cement Mixtures," Paper read before the Sydney Technical College Chemical Society 1914 (Vol. 1, pages 17—26). "Permeability of Concrete" (with the late B. J. Smart, B.Sc. (London), Paper read before the Engineering Association of New South Wales (Vol. xxxiii, Part 2, page 1). Have been engaged in the chemical and mechanical testing of all classes of structural materials in the Testing Laboratory, Public Works Department, New South Wales, for the past 27 years. These materials include Portland cement, steel, alloys, asphaltum, tars, paints, oils, etc. Representative of the Australian Chem. Institute on the Engineering Standardisation Committee dealing with the drawing up of a Standard Specification for Portland Cement for the Commonwealth of Australia. (*Signed by*) A. R. Penfold, R. Grant, Richard W. Challinor, Fred J. Berry, George Z. Du Pain.

MORRISON, FRANK RICHARD, Brae Street, Waverley, Sydney, N.S.W. Australia. Asst. Economic Chemist, Technological Museum, Sydney. Diploma in Chemistry of Sydney Technical College, 1921. Associate of Australian Chemical Institute since 1920. Member of Royal Society of N.S.W. since 1921. Member of Sydney Technical College Chemical Society since 1913, and Joint Hon. Secretary since 1921. *Positions held*: One year in laboratory of Sydney Technical College; three years in laboratory of Metropolitan Board of Water Supply and Sewerage, Sydney; nine years in present position at Technological Museum, Sydney. *Original papers*: "The Occurrence of Rutin in the leaves of the *Boronia* (N. O. Rutaceæ)" (read before the Royal Society of N.S.W., 2nd November, 1921); "The



essential oil of *Kunzea corifolia* " (read before the Royal Society of N.S.W., 1st November, 1922); "A Chemical examination of the seeds of the 'Bunya Bunya' (*Araucaria Bidwilli*, Hooker)" (read before the Royal Society of N.S.W., 3rd December, 1924). *Conjointly with Mr. A. R. Penfold, F.A.C.I., F.C.S.* "Preliminary note on a new stearoptene (probably a phenol ether) occurring in some essential oils of the Myrtaceae" (read before the Royal Society of N.S.W., 5th July, 1922); "The essential oil of *Eriostemon Crowei* (*Crowea saligna*) and the presence of a new phenol ether" (read before the Royal Society of N.S.W., 6th December, 1922); "Preliminary note on the electrolytic reduction of Piperitone" (read before the Royal Society of N.S.W., 5th September, 1923); "Notes on *Eucalyptus piperita* and its essential oils, with special reference to their Piperitone content" (read before the Royal Society of N.S.W., 2nd July, 1924). *Conjointly with Mr. A. Morrison*: "The chemical examination of the fixed oil of the Queensland Nut (*Macadamia ternifolia*)" (read before the Sydney Technical College Chemical Society, 24th June, 1923). (*Signed by*) A. R. Penfold, R. Grant, Richard W. Challinor, Fred J. Berry, George Z. Du Pain.

MURGATROYD, JOHN BLACKBURN, 90, St. George's Square, Westminster, S.W. 1. British. Demonstrator, Imperial College of Science and Technology, South Kensington. Taking up Research at the above College. (*Signed by*) H. B. Baker, J. N. Sugden, Leslie S. Theobald.

NANAVATI, CHITSUKHLAL HIRALAL, 80, Esplanade Road, Fort, Bombay. Hindoo. L.T.C., Analytical Chemist. Graduate of The Victoria Jubilee Technical Institute, Bombay; in Chemistry with special subject of Foods, Drugs and General Analysis; in Second Class with the title of Licentiate of Technical Chemistry, of the year 1921. Worked as Analytical Chemist with Messrs. Hughes & Davies and Messrs. Killick, Nixon & Co.; at present practising as Analytical Chemist. (*Signed by*) S. J. Sháh, Kapilram H. Vakil, R. G. Saraiya.

NICHOLSON, HENRY, "Aberlady," Osborne Rd., Stockton-on-Tees. English. Chemistry Master in Boys Secondary School, Stockton-on-Tees, since Nov. 1905. B.Sc. Durham University, 1904. M.Sc. for Research on the influence of the acetyl group as a protective agent in the oxidation of  $\alpha$ -acetylnaphthylamine, 1907. (*Signed by*) J. G. Taylor, J. A. Smythe, W. M. Madgin.

O'MEARA, ANNA MARIA, 83, Elsham Road, Holland Park, Kensington, W. 14. Irish. Pharmacist. M.P.S. (London). Was for 4 years trained under John Armstedt Ray, M.A., Ph.C., Trinity Coll., Dublin, at his Laboratory in 23, Nassau Street, but never took any Analytical Examination. Was 3 years Pharmacist at Bolingbroke Hospital, Wandsworth Common, S.W. 11; was 1 year at Willesden General Hospital as Pharmacist, and occasionally have worked at the M.A.B. Homerton and Park Royal, Hither Green. At present am pharmacist at the Women's Hospital, Soho Sq., and I take Students for both the qualifying and Apothecaries' Hall Exam. and train them for same. (*Signed by*) H. Lucas, A. Thomas, S. Greenberg.

PALMER, HORACE WINSTON, 15, Hollingdean Terrace, Brighton. British. Research Student, East London College. B.Sc. London, Hons. I, Chemistry. (*Signed by*) J. R. Partington, D. C. Jones, W. H. Patterson.

PARKER, NORMAN FREDERICK, 45, Sellons Avenue, Harlesden, N.W. 10. British (English). Chemical Engineer. B.A. Cambridge; Associate of Institute of Chemistry; 1st Class, Natural Science Tripos, Part II (Chemistry), 1923. (*Signed by*) W. J. Pope, C. T. Heycock, W. H. Mills.

PATTERSON, AUSTIN McDOWELL, Antioch College, Yellow Springs, Ohio,

U.S.A. United States. Professor of Chemistry, Antioch College, U.S.A. Formerly Editor of *Chemical Abstracts*. (Signed by) C. S. Gibson, T. Slater Price, John Greenaway.

PHILLIS, ERNEST, 22, Fairford Terrace, Dewsbury Rd., Leeds. British. Research Student, Leeds University. B.Sc., 1st Class Hons. in Pure Chemistry, 1925. (Signed by) J. B. Cohen, C. K. Ingold, P. K. Dutt, J. W. Baker.

POLLITT, JONATHAN, 17, Caversham Avenue, Palmers Green, N. 13. English. Chemistry Master, Hornsey County School, 1905-. B.A. (N.U.I.) Chemistry, Physics, Maths. Student (Chemistry) Birkbeck College since 1908. (Signed by) George Senter, Samuel Sugden, B. R. Heasman, F. J. Thorneycroft, A. M. Ward, Wm. W. Myddleton.

PORTER, CHARLES RAYMOND, 126, Linden Road, Bournville, Birmingham. English. Chemistry research assistant. M.Sc., A.I.C. Three years research assistant in Chemistry Department, University of Birmingham; part author of *Berichte*, 1925, 58, 333, and *J.C.S.*, 1924, 125, 731 and 1269. (Signed by) J. D. Main Smith, W. J. Hickinbottom, W. N. Haworth.

PRICE, EVAN EMBYS, Rock House, Heathfield, Swansea, Glam. British. Science Teacher, The College, Penarth, S. Wales. Graduate in Chemistry of University of Wales. Studied at University College, Swansea, 1920-1924. (Signed by) J. E. Coates, Leonard E. Hinkel, E. Stanley Hiscocks.

PRING, MARJORIE ELLEN, 86, St. Augustine's Avenue, S. Croydon, Surrey. British. Research Student at Bedford College for Women, Regent's Park. B.Sc., 1st Class Hons. in Chemistry, London University. (Signed by) J. F. Spencer, H. Crompton, M. S. Crewdson.

RÂY, JNANENDRA NATH, Calcutta. Indian. Lecturer, Calcutta University, M.Sc. (Cal.). Research Student, Manchester Univ. "Synthesis of oxyberberine" (joint author), *J.*, 1925, 127, 740; "Synthesis in the Thianthren series," *J.*, 1921, 119, 1959; "Catalytic action of Iodine in sulphonation," *J.*, 1920, 117, 1405; joint author, "Modification and extension of Friedel & Crafts' reaction," *J.*, 1920, 117, 1335. (Signed by) Robert Robinson, Arthur Lapworth, Henry Stephen, Wilson Baker.

ROBERTS, HERBERT CHARLES, 15, Estcourt Terrace, Headingley, Leeds. British. Chemist Director, Taylor's Drug Co., Ltd., P.O. Box 141, Burley Hill, Leeds. 20 years Analytical Chemist to above Co. Since 1908 Chemist Director and Superintendent under the Pharmacy Act to above Co. (Signed by) John Rennie, F. C. Savage, F. Pilkington Sargeant.

SANDERSON, PHYLLIS MARY, 7, Cresswell Place, S.W. 10. British. Research (Biochemical). I desire to become a member of this Society for the purpose of keeping in touch with current scientific investigations. (Signed by) F. G. Donnan, W. E. Garner, Henry Terrey.

SASS, ROSE RACHEL, Newnham College, Cambridge. British. Research Student. B.Sc. Hons. of the University of the Witwatersrand, Johannesburg, S. Africa. Demonstrator for 3 years. Now a research student in the Laboratory of Physical Chemistry, Cambridge University. (Signed by) T. M. Lowry, Eric K. Rideal, I. J. Faulkner.

SAXON, ROBERT, Westfield Terrace, Baildon, Yorks. British. Schoolmaster. Teacher of Chemistry at the Belle Vue Secondary School for 17 years. Teacher of Steam and Heat Engines, which included the Thermal Chemistry of Carbon and Hydrogen combustion and tests for  $\text{SH}_2$ ,  $\text{NH}_3$ , etc., in Coal and Producer Gas for 15 years in the Belle Vue Technical School (evening). Eleven years Head Master present School, The Forster School for Boys, Bradford, under the Bradford Authority; entrance to school only by

Scholarship Examination. Bachelor of Science, Victoria Univ., Manchester, 1896. Studies under Prof. Tilden, Royal Coll. of Science, London, 1900, and Prof. Watts, Geology, 1901 (Vacation Course). (*Signed by*) Barker North, Robt. D. Abell, T. W. Price.

SCIVER, ALBERT, 84, Vineyard Hill, Wimbledon Park, S.W. 19. English. Analytical and Consulting Chemist and Bacteriologist. B.Sc. (First Class Honours, University College, London), A.I.C. Assistant to Drs. S. and E. K. Rideal, 28, Victoria St., S.W. 1. Lecturer on Bacteriology applied to Chemistry at Battersea Polytechnic. (*Signed by*) F. G. Donnan, Eric K. Rideal, W. E. Garner.

SCOTT, GEORGE BATY, 37, Woodbridge Road, Knowle, Bristol. British. Organic and Inorganic Chemistry Student for two years at Central Polytechnic Institute, after passing the Qualifying Examination of Pharmaceutical Society, 1896. For some years have been closely associated with British Fine Chemicals, embracing Dye Intermediates, Research Chemicals, Saccharin and by-products. Wishful to have access to Society's Library and Publications, thus keeping up to date with the latest advances in Chemistry. (*Signed by*) J. Wicliffe Peck, D. Hughes, T. O. Kent, W. D. Wallace, Archibald Macpherson.

SCAMMELL, RUPERT BOSWOOD, c/o F. H. Faulding & Co., Ltd., Castle-reagh St., Redfern, Sydney, N.S.W. British. Manufacturing Chemist. Bachelor of Science (Sydney). Six years' experience in Manufacturing Chemistry with the above firm. I desire to keep in touch with modern chemical literature for research purposes. (*Signed by*) J. Kenner, George Harker, J. C. Earl.

SHIN, UPO, B.A.S., Agricultural Farm, Mandalay. Burman. Officiating Agricultural Chemist, Burma, Mandalay. Published as Memoirs of the Department of Agriculture in India on "The Phosphate Requirements of some Lower Burma Paddy Soils." (*Signed by*) Maung Ba, Maung Ba San, Maung Tun Tin.

SINGH, DALIP, near Tehsil, P.O. Lahore, India. Indian. Research Student, Cambridge University. Ph.D. Cambridge. (*Signed by*) W. J. Pope, W. H. Mills, Eric K. Rideal.

SMITH, FREDERICK FRANCIS PERCIVAL, Peterhouse, Cambridge. British. Research Student in the Cambridge Univ. Laboratories. 1st Class Nat. Sci. Tripos, Parts I and II. 1st Class London Ext. B.Sc. Hons. (in Chemistry). (*Signed by*) Hamilton McCombie, Harold A. Scarborough, W. A. Waters.

SMITH, ROBERT FREDERICK, 254, Higham Hill Road, Walthamstow, E. 17. British. Student of Chemistry at East London College. Desirous of keeping in touch with Modern Research. (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

SOPER, WILLIAM ERNEST, 50, Aislbie Road, Lee, London, S.E. 12. British. Research Student at East London College. B.Sc. (Lond.). (*Signed by*) J. R. Partington, E. E. Turner, Elwyn Roberts.

SOUTHERN, HERBERT KENNETH, Glenariff, Whaley Bridge, Nr. Stockport, Cheshire, also Government Laboratory, Strand, W.C. 2. British. Temporary Assistant Chemist, Government Laboratory. B.Sc. (Hons. Chem.) after 3 years and M.Sc. after a further year's research work in physical chemistry at Manchester University. Assistant Demonstrator in chemistry for 1 year at Manchester University. Six months as chemist with paint and enamel firm; 4 months at Government Laboratory. (*Signed by*) Robert Robertson, J. J. Fox, Geo. Stubbs, T. W. Harrison.

SPEIGHT, ERIC ALFRED, 61, Arthur Road, Wimbledon Park, S.W. 19.

British. Research worker in Organic Chemistry. Associateship of the Royal College of Science. B.Sc. (Lond.), Diploma of Imperial College, all in Chemistry. Have been engaged in study of Chemistry for 6 years, the last two being research. Published paper in Oct. 1924 *J.C.S.* on formation of Hydrindone derivatives. (*Signed by*) Jocelyn Thorpe, G. A. R. Kon, Arnold Stevenson.

SWIRE, FRANK HARLAND, 152, Queen's Road, Halifax, Yorks. British. Pharmacist. "Minor" Qualification of the Pharmaceutical Society. Member of the Pharmaceutical Society of Gt. Britain. Late Student in Chemistry at the Halifax Technical College and at The School of Pharmacy, Bloomsbury Sq., London, W.C. 1. (*Signed by*) T. E. Wallis, F. Browne, W. J. Stansfield.

TATTERSALL, HAROLD JAMES, B.Sc., Ph.D., 141, Thorold Road, Ilford, London, E. British. Research Chemist. Graduate of St. Andrews University. B.Sc., Ph.D. Research work carried out at University College, Dundee. Presently engaged in research photographic chemistry. Publishing under authorship McKenzie and Tattersall, probably in November 1925. (*Signed by*) Alex. McKenzie, O. Rhys Howell, R. Roger, John Foggie.

THORPE, WILLIAM VEALE, 270, Balham High Road, London, S.W. British. Research Student, Medical Research Council, Mount Vernon, Hampstead, N.W. 3. B.A. (Cambridge Natural Science Tripos, Parts I and II). One year's research at Mount Vernon. (*Signed by*) W. J. Pope, Jocelyn Thorpe, Hamilton McCombie, W. H. Mills.

TOWLER, WILLIAM MILBURN, 28, Denton Ave., Roundhay, Leeds. British. Student. B.Sc. Hons. Chemistry, Leeds University. (*Signed by*) H. M. Dawson, P. K. Dutt, H. Holness.

TRAILL, DAVID, 58, Chalmers St., Dunfermline, Scottish. Research Student. B.Sc. (1st Cl. Hons. Chemistry, St. Andrews), 1923. Research in Organic Chemistry, 1923-1925. Macbeth and Traill, *T.*, 1925, 127, 892; and 1118. (*Signed by*) A. Killen Macbeth, Irvine Masson, James Craik.

TRICKER, ELVERA ANNIE, 319, Norwich Rd., Ipswich. British. Student of Chemistry at Bedford College. (*Signed by*) J. F. Spencer, H. Crompton, J. Stewart.

TURNER, DONALD MORRISON, 40-42, Lexington St., W. 1. British. Representative of Mead Johnson & Co., Food Specialists. M.Am.Chem.Soc. Ten years Asst. Analyst, Govt. Laboratory, Newfoundland. Desire to receive the publications of the Society and keep in touch with modern work. (*Signed by*) D. James Davies, G. S. W. Marlow, F. S. Aumonier.

TURNER, GEOFFREY, 85, Winchester Avenue, Leicester. English. Research Student, attending Loughborough College, Leics. B.Sc. (2nd Class Honours, London); Diploma of Loughborough College (Honours). (*Signed by*) A. Bramley, A. T. Eggington, G. Lawton.

TYLER, NORMAN LEOPOLD, 9, St. Paul's Gardens, Spennymoor, Co. Durham. British. Chief Chemist and Manager of Messrs. Intermediates and Explosives, Ltd., Dean and Chapter Colliery, Ferryhill, Co. Durham. City and Guilds and South Kensington Examinations, Inorganic and Organic. South Staffs. Scholarship Metallurgy., Iron and Steel. Secretary of N.E. Section of the British Association of Chemists. Fourteen years with Messrs. Chance and Hunt, Ltd., Oldbury and Wednesbury. Chemist in Charge of several plants for eight years. (*Signed by*) S. I. Levy, L. R. B. Pearce, W. A. S. Calder.

VERNON, HERBERT WARD, 245, Albert Rd., London, N. 22. British. Research Chemist. B.Sc. in Hons. Chemistry of Victoria University, Manchester. Held post as Research Chemist for last nine years. (*Signed by*) Percy C. C. Isherwood, B. H. Bowles, R. E. Brett.

WEBB, FREDERICK HENRY, "St. Malo," Jameson Road, Harpenden. British. Manufacturing Chemist and Optician. (1) Early Education at the Dunstable Grammar School. (2) Studied Analytical Chemistry under J. B. Hoblyn, B.Sc., F.I.C. (3) Studied Chemistry and Physics at the London School of Chemistry under Henry Wootton, B.Sc. (4) Passed the Qualifying Examination of the Pharmaceutical Society in 1910. (5) Passed the Qualifying Examination as a Fellow of the National Association of Opticians in 1923. Particularly interested in Analytical and Scientific work. (*Signed by*) Frank B. Arnold, J. J. Laws, Percy Barrs.

WILLIAMS, EWART HARROD, 31, Thornsbeach Road, Catford, S.E. 6. British. Chemist, Government Laboratory, Clement's Inn Passage, W.C. B.Sc. (Hons. Lond.), A.C.G.F.C., A.I.C. Research work at Finsbury Technical College with Prof. A. J. Hale, and at the Government Laboratory with Dr. J. J. Fox. I desire to keep in touch with modern developments in Pure and Applied Chemistry, through the Society's Journal, and by attending the Scientific Meetings of the Society. (*Signed by*) Robert Robertson, Geo. Stubbs, J. J. Fox, A. G. Francis.

WILLIAMS, GWYN, Cae Ffynnon, Llandudno Junction, North Wales. Welsh. Research Student in Chemistry at University College of North Wales, Bangor. 1924, B.Sc. (Wales) with 1st Class Hons. in Chemistry. 1924-5, Research Student at University College, Bangor. (*Signed by*) Kennedy Orton, F. G. Soper, H. B. Watson.

WILLIAMS, HUGH AMPHLETT, 249, Kennington Rd., S.E. 11. English. Student. Student of the Institute of Chemistry, desiring the use of the Library and the Periodicals. (*Signed by*) George A. Stokes, Ernest W. Wright, A. J. Hale, H. M. Atkinson.

WILLIAMS, ROBERT HARDING, 131, Anlaby Road, Hull. British. Chemist (Pharmaceutical), practising as a Chemist at above address. (Leeds University Matric.). Two years at Swansea Municipal College (3rd year Medical Student). M.P.S. (1907). One year Hull Technical College. Was 2 years as Chemist in Middlesbro' (Analytical), and have been in business at above address nearly 4 years. Have been doing analytical work for a number of years. (*Signed by*) Harry Thompson, Thos. A. Nightscales, Edward Chapman.

WILTSHIRE, JOHN LAURENCE, 36, Fordel Road, Catford, London, S.E. 6. English. Assistant Works Chemist to Messrs. Burt, Boulton, and Haywood, Coal Tar Distillers, London. B.Sc. London, 2nd Class Honours in Chemistry (1925). Three years' experience with consulting analyst (Mr. F. W. Harbord). Now occupied as above and in pure chemical research under Mr. E. de B. Barnett at the Sir John Cass Technical Institute, London. (*Signed by*) E. de Barry Barnett, Marcus A. Matthews, James W. Cook.

WOLFE, JOHN JAMES BENJAMIN, 24, Greyhound Road, Hammersmith, W. 6. English. Student (Research), East London College. (*Signed by*) J. R. Partington, Elwyn Roberts, D. C. Jones.

WRIGHT, GORDON MITCHELL, University Chemical Labs., Cambridge. British. Research Chemist. M.A. (Cantab.), B.Sc. (Glasgow). (*Signed by*) Hamilton McCombie, A. C. P. Lunn, Harold A. Scarborough.

WYATT, WILFRED FISHER, North Anston, Nr. Sheffield. British. Demonstrator in Chemistry, the University of Sheffield. B.Sc. Hons. Chemistry, 1923, Sheffield University; M.Sc., 1924, Sheffield University. (*Signed by*) W. P. Wynne, F. G. Tryhorn, G. M. Bennett, Arthur W. Chapman.

ZIMMERMANN, JOHN FREDERICK, 17, Stile Hall Gardens, Chiswick, W. 4. British. Research Chemist. Diploma of Engineer Chemist, Zurich Poly-

technicum. 2½ Years as Assistant to Dr. Tcherniac. (*Signed by*) J. Tcherniac, A. G. Bloxam, C. S. Gibson.

The following Certificates have been authorised by the Council for presentation to ballot under Bye-Law I (2).

CUTBERT, BERTRAM, c/o The British Australian Cotton Assocn., Oil Mills, Brisbane, Australia. British. Oil Mills Manager. 1906-1912, Analytical Chemist, The Hull Oil Manuf. Co., Ltd., Hull, Eng. 1912-1914, Research Chemist, The Hull Oil Manuf. Co., Ltd., Hull, Eng. 1914-1919, Research Chemist and Refinery Manager for the Hull Oil Manuf. Co., Ltd. 1920-1923, Assistant Works Manager and Soap Works Manager for the Hull Oil Manuf. Co., Ltd. 1923 to present time, Oil Mills Manager for the British Aust. Cotton Assocn., Ltd., Brisbane, Queensland, Australia. (*Signed by*) Geo. H. Appleyard, H. W. Potts.

MILLER, EDGAR CALVIN LE ROY, c/o Medical College of Virginia, Richmond, Va., U.S.A. English. Teacher in Medical College of Virginia. Professor of Biological Chemistry and Bacteriology. M.D. (University of Michigan). Secretary of the Virginia Academy of Science. Past secretary and past chairman of the Virginia Section of the American Chemical Society. (*Signed by*) F. P. Dunnington.

SIGOT, ALBERT LOUIS AUGUSTE, Institut de chimie, 2, Rue Goethe, Strasbourg. Français. Licencié és Sciences, préparateur à la Faculté des Sciences de l'Université de Strasbourg. Chargé des travaux pratiques de Chimie Physique. (*Signed by*) Louis Hackspill, Georges Baume.

## ADDITIONS TO THE LIBRARY.

### I. *Donations.*

ABDERHALDEN, EMIL. [Editor.] Handbuch der biologischen Arbeitsmethoden. Abt. I. Chemische Methoden, Teil 2, Heft i. Berlin 1925. pp. 456. M. 21. (*Recd.* 2/11/25.)

From the Publishers: Herren Urban & Schwarzenburg.

BARBAUDY, JEAN. Contribution à l'étude de la distillation des mélanges ternaires hétérogènes. Paris 1925. pp. iv + 156. ill. (*Recd.* 11/11/25.)

From the Author.

EUCKEN, ARNOLD. Fundamentals of physical chemistry. Translated and adapted from the 2nd German edition by ERIC R. JETTE and VICTOR K. LAMER. New York 1925. pp. xxiv + 700. ill. 27s. 6d. net. (*Recd.* 12/11/25.)

From the Publishers: The McGraw-Hill Publishing Co.

JOURNAL OF THE CHEMICAL INDUSTRY. Vol. I, etc. Moscow 1924 +. [In Russian.] (*Reference.*) From Dr. M. Nierenstein.

KOPACZEWSKI, W. Introduction à l'étude des colloïdes: état colloïdal et ses applications. Paris [1925]. pp. viii + 226. ill. 16 fr. (*Recd.* 2/11/25.)

From the Publishers: MM. Gauthier-Villars et Cie.

LEVENE, P. A. Hexosamines and mucoproteins. London 1925. pp. x + 164. 10s. 6d. net. (*Recd.* 22/10/25.)

From the Publishers : Messrs. Longmans, Green & Co.

MASSON, IRVINE. Three centuries of chemistry : phases in the growth of a science. London 1925. pp. 192. ill. 10s. 6d. net. (*Recd.* 3/11/25.) From the Publishers : Messrs. Ernest Benn.

NAGAOKA, HANTARO. Anniversary volume. By his friends and pupils on the completion of 25 years of his Professorship. Tokyo 1925. pp. xvi + 424. ill. From the Tokyo Imperial University.

RUSSIAN PHYSICAL AND CHEMICAL SOCIETY. Journal. [Chemical Section.] Vol. 55, part 5, etc., Leningrad 1924 +. [In Russian.] (*For circulation.*) From Dr. M. Nierenstein.

THOMS, HERMANN. [Editor.] Handbuch der praktischen und wissenschaftlichen Pharmazie. Vol. III. Part iv. Vol. IV. Part ii. Berlin 1925. pp. [288], [272]. ill. M. 20. (*Recd.* 2/11/25.)

From the Publishers : Herren Urban & Schwarzenberg.

WEST, CLARENCE JAY, and BEROLZHEIMER, D.D. Bibliography of bibliographies on chemistry and chemical technology 1900—1924. (Bulletin of the National Research Council, No. 50.) Washington, D.C. 1925. pp. 308. (*Reference.*) \$2.50 net.

From the Publishers : The National Research Council.

## II. By Purchase.

ARNOU, CH. Les industries de la conservation des fruits. 3 parts. Vannes 1925. pp. 356, 280, 142. ill. 55 fr. (*Recd.* 5/11/25.)

ARRHENIUS, SVANTE AUGUST. Chemistry in modern life. Translated by CLIFFORD SHATTUCK LEONARD. New York 1925. pp. xvi + 286. ill. 13s. 6d. net. (*Recd.* 10/11/25.)

DELBRÜCK, MAX. Illustriertes Brauerei-Lexikon. 2nd edition. 2 vols. Edited by F. HAYDUCK. Berlin 1925. pp. iv + 534, ii + 438. ill. (*Reference.*) M. 54.

GAMBER, OSWALD. Die Herstellung des Cereisens und die Gewinnung der Chloride der seltenen Erden. Wien 1925. pp. viii + 126. M. 4. (*Recd.* 26/10/25.)

GARDNER, HENRY A. Physical and chemical examination of paints, varnishes, and colors. 2nd edition. Washington, D.C. 1925. pp. 376. ill. [Together with 22 circulars of the U.S. Standards Specification Board.] 45s. net. (*Recd.* 19/10/25.)

GRÜN, ADOLF. Analyse der Fette und Wachse sowie der Erzeugnisse der Fettindustrie. Vol. I. Berlin 1925. pp. xii + 576. ill. M. 36. (*Recd.* 22/10/25.)

IHERING, ALBRECHT VON. Maschinenkunde für Chemiker. 3rd edition. pp. viii + 348. ill. M. 18. (*Recd.* 27/10/25.)

KLING, ANDRÉ. [Editor.] *Méthodes actuelles d'expertises employées au Laboratoire Municipal de Paris et documents sur les matières relatives à l'alimentation.* 6 vols. Paris 1921—1923. (Recd. 4/11/25.)

LANGE, OTTO. *Die Schwefelfarbstoffe.* 2nd edition. (Chemische Technologie in Einzeldarstellungen.) Leipzig 1925. pp. xiv + 371. ill. *M.* 28. (Recd. 26/10/25.)

OSTWALD, [WILHELM], and LUTHER [ROBERT THOMAS DIEDRICH]. *Hand- und Hilfsbuch zur Ausführung physikochemischer Messungen.* 4th edition. Edited by CARL DRUCKER. Leipzig 1925. pp. xx + 814. *M.* 35. (Recd. 27/10/25.)

PREUSS, E. *Die Fabrikation des Stärkezuckers, des Stärkezuckersirups und der Zuckerkulör mit besonderer Berücksichtigung des Betriebes.* Leipzig 1925. pp. xvi + 320. ill. *M.* 16.20. (Recd. 27/10/25.)

STAUB, H. *Insulin: Darstellung, Chemie, physiologische und therapeutische Anwendung.* 2nd edition. Berlin 1925. pp. vi + 178. ill. *M.* 8.40. (Recd. 3/11/25.)

### III. Pamphlets.

MINES DEPARTMENT. *Safety in Mines Research Board.* Paper No. 13. *Stone dust as a preventive of coal dust explosions. Comparative tests.* By G. S. RICE and RICHARD VERNON WHEELER. London 1925. pp. 15. ill.

RAY, SIR PRAFULLA CHANDRA. *Acharyya Prafulla Chandra Ray and his many-sided activities.* By an admiring pupil. Calcutta 1924. pp. vi + 79. ill.

RAY, PRIYADA RANJAN. *Chemical research in India.* (From the *Calcutta Review*, 1925.)

SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. *Report of test by the Director of Fuel Research on Parker low temperature carbonisation plant installed at Barugh, Barnsley, at the works of Low Temperature Carbonisation, Ltd. Test carried out July 22nd to 24th, 1924.* London 1924. pp. iv + 24. ill.

— *Report of test by the Director of Fuel Research on the carbonisation plant of Midland Coal Products, Ltd., Netherfield, Nottingham. Tests carried out January 20th to 23rd, 1925.* London 1925. pp. vi + 23. ill.

— *River gauging: a report on methods and appliances suitable for use in Great Britain.* By M. A. HOGAN. London 1925. pp. viii + 80. ill.

— *First Report of the Fabrics Co-ordinating Research Committee.* London 1925. pp. iv + 70. ill.



SCIENTIFIC AND INDUSTRIAL RESEARCH, Department of. Deterioration of structures of timber, metal, and concrete exposed to the action of sea-water. Fifth (interim) report of the Committee of the Institution of Civil Engineers. Edited by P. M. CROSTHWAITE and GILBERT R. REDGRAVE. London 1925. pp. viii + 66. ill.

— *Building Research Board*. Bulletin No. 1. Jointless (magnesium oxychloride) floors. By P. W. BARNETT and B. BAKEWELL. London 1925. pp. iv + 26. ill.

— *Food Investigation Board*. Special Report No. 21. The "gas" content and ventilation of refrigerated holds carrying apples. (Second Report on the Australian Expedition, 1923.) London 1925. pp. iv + 36. ill.

— — Special Report No. 22. Brown heart in Australian apple shipments. (Third Report on the Australian Expedition, 1923.) London 1925. pp. vi + 28. ill.

— — Special Report No. 23. Functional diseases of apples in cold storage. By FRANKLIN KIDD and CYRIL WEST. London 1925. pp. 15 + xiii plates.

— — Special Report No. 25. The handling and transport of fish. By EDGAR GRIFFITHS and CRAWFORD HERON. London 1925. pp. iv + 25. ill.

— *Fuel Research Board*. Fuel for motor transport. Third memorandum. Power alcohol from tuber and root crops in Great Britain. London 1925. pp. vi + 37.

— — Physical and chemical survey of the national coal resources, No. 4. The Lancashire coalfields: the Ravine seam. Part i. London 1925. pp. vi + 34.

— — Technical Paper No. 11. The microstructure of a coal seam. By JAMES LOMAX. London 1925. pp. iv + 14 + 24 plates.

— — Technical Paper No. 12. The heating of rooms: a comparison of the costs of different methods on the basis of warmth comfort. By MARGARET WHITE FISHENDEN, assisted by ROBERT ERNEST WILLGESS. London 1925. pp. iv + 48.

— — Technical Paper No. 13. The domestic grate: an experimental investigation of the relation between the design of a grate and the heat radiated into a room. By MARGARET WHITE FISHENDEN. London 1925. pp. iv + 25. ill.

— — Technical Paper No. 14. The enrichment of coal gas by the injection of oil into the retorts during carbonisation. London 1925. pp. vi + 61. ill.

SHARP, PAUL FRANCIS, and GORTNER, ROSS AIKEN. Viscosity as a measure of hydration capacity of wheat flour and its relation

to baking strength. (*Univ. Minnesota Agric. Exper. Station, Technical Bulletin No. 19.*) St. Paul 1923. pp. 119. ill.

SIMONSEN, JOHN LIONEL. The constituents of some Indian essential oils. Parts XIII—XV. (From the *Indian Forest Records*, 1924, 11.)

SIMPKIN, NEVILLE, and DAWE, ALFRED. Boiler feed water (supply, softening and control in colliery practice). (*Lancs & Cheshire Coal Research Assoc. Bulletin No. 16.*) London 1925. pp. 45.

UNITED STATES. *Department of Agriculture.* Department Bulletin No. 1323. Citrus pectin. By HOMER D. POORE. Washington 1925. pp. 19.

— *Department of Commerce.* Bureau of Standards. Technologic Paper No. 273. Performance tests of a liquid laundry soap used with textile materials. By F. R. MCGOWAN, F. W. SMITHER, and CHARLES W. SCHOFFSTALL. Washington 1924. pp. 26. ill.

WOODMAN, ROWLAND MARCUS. The physics of spray liquids. I. The properties of wetting and spreading. (From the *J. Pomology and Horticultural Science*, 1924, 4.)

WORLEY, FREDERICK PALLISER. A new view of atomic structure and the relationship of the chemical elements. (From the *Rept. Austral. Assoc. Adv. Sci.*, 1923, 16.) ill.

WOTCHAL, EUGEN PH. A contribution to the study of wood-sap. Moscow 1916. pp. 72. ill. [In Russian, with an English summary.]

# PROCEEDINGS

## OF THE

# CHEMICAL SOCIETY.

Informal Lecture, Thursday, November 26th, 1925, at 6 p.m.,  
Dr. N. V. SIDGWICK, M.A., F.R.S., Vice-President, in the Chair.

The CHAIRMAN mentioned that this was the first of the Informal Lectures to be given by the Society, and then called upon Professor R. Robinson, D.Sc., F.R.S., to deliver his Lecture entitled: "Recent Research on the Structural Relationships of some Plant Products."

At the conclusion of the Lecture a Vote of Thanks to the Lecturer was proposed by Professor T. M. Lowry, seconded by Dr. R. H. Pichard, and carried with acclamation, Professor Robinson making due acknowledgment.

Ordinary Scientific Meeting, Thursday, December 3rd, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., LL.D., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows:

	Elected.	Died.
James Kerr Erskine .....	Dec. 5th, 1889.	April, 1925.
Robert Walter Oddy .....	May 15th, 1890.	Nov. 24th, 1925.
William Robert Lang .....	March 4th, 1897.	Nov. 20th, 1925.

Certificates were read for the first time in favour of:

Dattatraya Vishwanath Bal, Rothamsted Experimental Station, Harpenden.  
Bernard Meredith Brown, B.Sc., F.I.C., Hill Close, Croham Manor Road,  
S. Croydon.

Frederick Leslie Clark, 170, Barnsley Road, Sheffield.

Reginald Clifford Fawcett, B.Sc., The Cottage, Pentre, Wrexham.

Ko Ko Gyi, Agricultural College, Mandalay.

Tom Heap, B.Sc., Birch Mount, Church Road, New Mills, Stockport.

Stanley Barker Johnson, c/o Colombo Gas & Water Co., Ltd., Colombo,  
Ceylon.

Leonard George Jupp, B.Sc., A.R.C.S., 6, Chesham Road, Kemp Town,  
Brighton.

Horace Alfred Mayes, B.Sc., The Cottage, Sewage Works, Vicarage Lane,  
East Ham, E. 6.

Henry Geoffrey Ordish, B.A., Chilcombe, Milton Road, Harpenden.  
 Arnold Piukus, 238, Amhurst Road, Stoke Newington, N. 16.  
 Clifford Burrough Purves, B.Sc., Edenbank, Cupar.  
 Suresh Chandra Ray, P.O. Alambazar, Ray Villa, Calcutta.  
 Edna Clark Smith, B.Sc., 9, Gilston Road, S.W. 10.  
 Sidney David Sutton, 2, Glasshouse Street, W. 1.  
 Raymond Taylor, M.A., B.Sc., St. Brelades, Woodside Road, Parkstone.  
 Richard Victor Thomas, B.A., 17, Pretoria Road, Cambridge.  
 Henry Wilkins, B.Sc., 13, Kinfauns Road, Goodmayes.  
 Reginald Frank Wright, A.R.C.S., Fairhazel, Avondale Road, Hove.

Messrs. E. Horton and W. B. Saville were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared elected as Fellows :

Robert Leslie Andrew.	Eric Bertram Evans, B.Sc.
Louis Baissac.	Elinor Katharine Ewbank, B.A.
William Francis Barker, Ph.D.	Elizabeth Monica Openshaw Farrow,
Ralph Basden.	M.A.
Frank Bell.	Oliver Free, B.A.
Arthur Neville Copnall Bennett, B.Sc.	William Marshall Freeman.
Harold Frederick Betts, B.Sc.	Eva Florence Gee.
John Cecil Bird, B.Sc., A.I.C.	James Walter Shanks Gemmell, B.Sc.
Lionel Christopher William Birkett,	Francis Reginald Glover.
B.Sc.	William Bouch O'Brien Goudielock.
James Boyd, F.I.C.	Felix John Theodore Grigg, M.Sc.,
Frank Symonds Bradhurst.	A.I.C.
Edward Britnell, B.Sc.	George Vincent Hall, B.Sc.
Reginald John Bromfield.	John Hall, M.Sc., A.I.C.
Francis Hereward Burstall, B.Sc.	William Rowan Hare.
Archer John William Butterfield.	Walter Healey.
John Hildred George Carlile, B.Sc.,	Thomas Henderson, M.C., M.A., B.Sc.
A.R.C.S.	Herbert Sim Hirst.
Leslie James Chalk, B.Sc.	Syed Husain, M.Sc.
Rama Charan, B.Sc., B.Sc.Tech.	Toru Iwadare.
John William Corran, B.Sc., Ph.D.,	David Christopher Mendis Jaye-
A.I.C.	wardene.
John Harold Cottier.	Gilbert Jessop, M.Sc., Ph.D.
Edward Mortimer Crowther, D.Sc.,	Charles Benjamin Johnson.
F.I.C.	Walter Idris Jones, B.Sc., Ph.D.
Bertram Cuthbert.	Henry Wilfrid Keenan.
Frank Edwin Dickinson.	Brian Charles Lavers Kemp, B.A.
Joseph Raymond Dolphin, B.Sc.	Charles King.
William Donovan, M.Sc.	Frederick Karl Victor Koch, B.Sc.,
John Stanley Dunn, M.A., Ph.D.,	A.R.C.S.
A.I.C.	Charles Dudley Langford, B.Sc.,
John Horsfall Dyde.	A.R.C.S.
George Malcolm Dyson, B.A., B.Sc.,	Banarsi Das Laroia, B.A., B.Sc.
Ph.D.	Henry Guinness de Laszlo, B.A.,
Alfred Eccles, B.Sc.	Ph.D.
Edwin Francis Edwards.	Bertram Grey Leatherbarrow.
John Moelwyn Edwards.	Sam Lenher, B.A.
George Albert Elliott, M.Sc.	John Joseph Lennon, M.Sc.

- |                                      |                                       |
|--------------------------------------|---------------------------------------|
| William Macartney.                   | Albert Seiver, B.Sc., A.I.C.          |
| Ivan Roy McHaffie, B.A., M.Sc.       | George Baty Scott.                    |
| Neil McLean, M.A., B.Sc.             | Upo Shin.                             |
| Leslie George Manchester, B.Sc.      | Albert Louis Auguste Sigot.           |
| William Alfred Nottage Markwell.     | Dalip Singh, Ph.D.                    |
| William Francis Martin, F.I.C.       | Frederick Francis Percival Smith,     |
| Charles Henry Lawrence Miller, B.Sc. | B.A., B.Sc.                           |
| Edgar Calvin le Roy Miller, M.D.     | Robert Frederick Smith.               |
| Arthur Moore.                        | William Ernest Soper, B.Sc.           |
| Alexander John Morrison.             | Herbert Kenneth Southern, M.Sc.       |
| Frank Richard Morrison.              | Eric Alfred Speight, B.Sc.            |
| John Blackburn Murgatroyd.           | Frank Harland Swire.                  |
| Chitsukhlal Hiralal Nanavati.        | Harold James Tattersall, B.Sc., Ph.D. |
| Henry Nicholson, M.Sc.               | William Veale Thorpe, B.A.            |
| Anna Maria O'Meara.                  | William Milburn Towler, B.Sc.         |
| Horace Winston Palmer, B.Sc.         | David, Traill, B.Sc.                  |
| Norman Frederick Parker, B.A.,       | Elvera Annie Tricker.                 |
| A.I.C.                               | Donald Morrison Turner.               |
| Austin McDowell Patterson.           | Geoffrey Turner, B.Sc.                |
| Ernest Phillis, B.Sc.                | Norman Leopold Tyler.                 |
| Jonathan Pollitt, B.A.               | Herbert Ward Vernon, B.Sc.            |
| Charles Raymond Porter, M.Sc.,       | Frederick Henry Webb.                 |
| A.I.C.                               | Ewart Harrod Williams, B.Sc., A.I.C.  |
| Evan Emrys Price, B.Sc.              | Gwyn Williams, B.Sc.                  |
| Marjorie Ellen Pring, B.Sc.          | Hugh Amphlett Williams.               |
| Jnanendra Nath Rây, M.Sc.            | Robert Harding Williams.              |
| Herbert Charles Roberts.             | John Laurence Wiltshire, B.Sc.        |
| Phyllis Mary Sanderson.              | John James Benjamin Wolfe.            |
| Rose Rachel Sass, B.Sc.              | Gordon Mitchell Wright, M.A., B.Sc.   |
| Robert Saxon, B.Sc.                  | Wilfred Fisher Wyatt, M.Sc.           |
| Rupert Boswood Scammell, B.Sc.       | John Frederick Zimmermann.            |

The following papers were read :

- "On the Budde effect in bromine. Part I. The photoactive constituent in wet bromine." By B. LEWIS and E. K. RIDEAL.
- "On the Budde effect in bromine. Part II. The kinetics of the reaction and the light absorption of wet and dry bromine." By B. LEWIS and E. K. RIDEAL.
- "The influence of carbon rings on the velocity of reactions involving their side-chains. Part I. The hydrolysis of cyclic and open-chain malonic esters." By R. GANE and C. K. INGOLD.
- "The density of boric oxide glass and the suspected variation in the atomic weight of boron." By H. V. A. BRISCOE, P. L. ROBINSON, and G. E. STEPHENSON.

Ordinary Scientific Meeting, Thursday, December 17th, 1925, at 8 p.m., Dr. ARTHUR W. CROSSLEY, C.M.G., C.B.E., LL.D., F.R.S., President, in the Chair.

The PRESIDENT referred to the loss sustained by the Society, through death, of the following Fellows :

	<i>Elected.</i>	<i>Died.</i>
George Frederick William Blackburn .....	May 15th, 1913.	Nov. 23rd.
Edmund Knecht .....	Dec. 1st, 1910.	Dec. 8th.
James Grant .....	Feb. 6th, 1890	Dec. 7th.

The PRESIDENT announced that :

1. A Special Lecture will be delivered by Professor J. Barcroft, F.R.S., entitled "Hæmoglobin" on Thursday, February 11th, 1926, at 8 p.m. The Lecture will be held in the Chemistry Theatre of the University College, Gower Street, W.C. 1, by the kind permission of the College Authorities.

2. British Chemical Abstracts "A," Pure Chemistry for 1926, printed on one side of the paper only, and gummed or ungummed, will be obtainable by Fellows at the price of £3 0s. 0d., post free. Application should be made to the Assistant Secretary, Mr. S. E. Carr, as soon as possible.

The following were formally admitted Fellows of the Chemical Society : Thomas M. Sharp, Arthur Moor, Cecil J. May, J. F. Zimmermann, F. Bell, C. D. Langford, and J. M. Edwards.

Certificates were read for the first time in favour of :

Edwin Melhuish Bailey, Almond Hill, Pumpherston, Midcalder.  
 Carl Howard Collie, B.A., New College, Oxford.  
 William Eric Downey, Ph.D., Imperial College of Science and Technology, S. Kensington, S.W. 7.  
 Andor Fodor, Ph.D., Hebrew University, Jerusalem.  
 Herbert Harris, B.Sc., Ph.D., A.R.C.S., 1, Royal York Villas, Clifton, Bristol.  
 Ralph Harry Klein, A.I.C., 11, Park Place Villas, Maida Hill, W. 2.  
 Montague Alexander Phillips, A.I.C., 31, Cator Street, S.E. 15.  
 Devasikhamani Sunderavelu Pillai, 37, Hill Street, Stoke-on-Trent.  
 Charles Aylmore Ray, B.A., 47, Somerford Grove, Tottenham, N. 17.  
 Ivy Winifred Elizabeth Rogers, 8, St. Lawrence Road, W. 10.  
 Ronald Stanley Russell, B.A., 47, Redington Road, Hampstead, N.W. 3.  
 Robert John Schaffer, B.A., B.Sc., 3, Hambalt Road, S.W. 4.  
 Charles Richard Noël Strouts, B.A., B.Sc., A.I.C., Westminster Bank, Kew Gardens, Surrey.  
 Frank Sherwood Taylor, M.A., B.Sc., 21, Shortlands Road, Shortlands, Kent.  
 Claude Stanley Watson-Will, Musgrave Road, Indooroopilly, Brisbane.  
 Idris Williams, B.A., 19, Silver Street, Cambridge.

The meeting was then adjourned, and the Informal Meeting declared open.

The Council has made the following Grants from the Research Fund :

	£	s.	d.
Preparation and investigation of rare earth carbides. N. L. Anflogoff ... ..	10	0	0
Preparation of phenanthrenes from stilbenes. J. N. Ashley ...	5	0	0
Investigation of certain binary and ternary systems. C. R. Bailey ... ..	5	0	0
Synthesis of genistein. W. Baker ... ..	15	0	0
Studies in the anthracene series ( <i>contd.</i> ). E. de B. Barnett ...	5	0	0
(a) Studies in aliphatic and cyclic sulphides ... ..			
(b) Reactivity of some quinoxaline bases. G. M. Bennett ...	5	0	0
Study of the mutual solubility relations of certain binary liquid systems. H. F. Betts ... ..	3	0	0
The dynamic isomerism of menthyl-cotarnine and of asymmetrical xanthidrols. B. C. Chatterjee ... ..	12	0	0
Thiocyano- and selenocyano-groups in the aromatic nucleus. F. Challenger ... ..	5	0	0
Preparation and study of certain polyhydroxy derivatives of diphenic acid. G. H. Christie ... ..	5	0	0
Synthesis of substituted tri- and tetra-methylene ring derivatives from compounds obtained by condensation of malonic ester with aldehydes. H. Clayton ... ..	5	0	0
Anthranyl ketones. J. W. Cook ... ..	5	0	0
Addition of bivalent carbon compounds to bodies of the diazo-methane class. K. Cooper ... ..	5	0	0
Stability of Schiff's bases. P. K. Dutt ... ..	5	0	0
Conversion of asymmetric bromo compounds into the corresponding sulphonic acids. E. B. Evans ... ..	5	0	0
Influence of the benzoyl group on the mobility of the three-carbon tautomeric system. M. D. Farrow ... ..	10	0	0
Studies in the catalytic activity of charcoal. J. B. Firth ...	10	0	0
Solubility relationships of alums and pseudo alums. S. Glasstone	3	0	0
Study of alkylene thiosulphates and of alkylene disulphonic acids. J. Goodspeed ... ..	5	0	0
Quasi-aromatic structure ( <i>contd.</i> ). F. R. Goss ... ..	5	0	0
Properties of conjugated compounds. A. T. Healey ... ..	6	0	0
Periodic chemical reactions. E. S. Hedges ... ..	15	0	0
Substitution in the aromatic nucleus. W. J. Hickinbottom ...	4	0	0
Photochemical combination of hydrogen with other gases. H. S. Hirst ... ..	7	0	0
(a) Synthetical experiments in the anthocyanidin series ...			
(b) Synthesis of indole derivatives. H. R. Ing ... ..	10	0	0
Conditions of equilibrium between alkali and alkaline earth halides and the alcohols ( <i>contd.</i> ). W. J. Jones ... ..	8	0	0
The chemistry of the three-carbon system. L. G. Jupp ...	8	0	0
(a) Reaction with ammonia of various unsaturated cyano esters			
(b) Methylation and ethylation products of various unsaturated cyano amides. (Miss) W. Kilroy ... ..	5	0	0
Lactone formation from the $\alpha\alpha'$ - $\beta\beta'$ -dibromo adipic acids. C. D. Langford ... ..	6	0	0
Properties of conjugated compounds. B. D. Laroia ... ..	6	0	0
Substituted diphenyl compounds. R. J. W. Le Fèvre ... ..	5	0	0

	£	s.	d.
Condition of formation and stability of carbon rings. J. J. Lennon ... ..	8	0	0
Action of nitric acid on unsaturated hydrocarbons. (Miss) P. V. McKie ... ..	10	0	0
Synthesis of (a) Degradation product of brucine, and (b) Harmaline and some of its derivatives. R. H. F. Manske ...	10	0	0
The effect of bulky groups on the mobility of the 3-carbon system. C. J. May ... ..	5	0	0
Researches on thallium compounds ( <i>contd.</i> ). R. C. Menzies ...	8	0	0
Three carbon tautomerism. B. T. Narayanan ... ..	6	0	0
Kinetics of the induction period of the hydrogen-chlorine reaction with ultra-violet light. R. G. W. Norrish ... ..	10	0	0
Action of ozone on dry iodine. H. W. Palmer ... ..	5	0	0
Nitration of substituted phthalides. J. N. Rây ... ..	7	0	0
Reactions between 1 : 3-diketones and amino and amido bodies. E. Roberts ... ..	5	0	0
Investigation of certain sesquiterpenes. J. M. Robertson ...	5	0	0
Properties of unsaturated cyclic ketones. J. Ross ... ..	5	0	0
The direct introduction of substituents into a mono-substituted diphenyl. H. A. Scarborough ... ..	5	0	0
Preparation and properties of various types of halogenated naphthalene derivatives. J. B. Shoesmith ... ..	10	0	0
Researches on sulphuryl chloride and chlorination. O. Silberrad	5	0	0
Influence of substituents on the stability of certain spiro and associated ring systems. S. S. G. Sircar ... ..	6	0	0
The basic salts, salts of mixed acids, and complex salts of metals of the 3rd and 8th periodic groups. J. D. Main Smith ...	12	0	0
Nitration studies of tertiary aromatic amines. J. M. Smith ...	5	0	0
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Introduction of the methylene-dioxy group and of similar groups into the aromatic nucleus. V. M. Trikojus ... ..	8	0	0
Conversion of substituted aromatic amines into quinolines. E. E. Turner ... ..	5	0	0
Effect of polar substituents on the Walden inversion among benzene derivatives. E. E. Turner ... ..	5	0	0
The chemistry of molybdenum. W. Wardlaw ... ..	5	0	0
Reaction of halogens with aliphatic acids, anhydrides, and allied substances. H. B. Watson ... ..	5	0	0
(a) Spatial structure of cycloparaffins ... ..			
(b) Constitution of the mono-chloro- and mono-bromo-methyl succinic acids. W. A. Wightman ... ..	5	0	0
(a) The migratory aptitudes of methoxy-phenyl groups ...			
(b) Experiments upon phthalophenone derivatives, etc. E. W. Wignall ... ..	10	0	0
Structural mobility in dihydromuconic systems. R. F. Wright .	5	0	0
Total ... ..	£388	0	0



List of papers, or abstracts thereof, received between November 20th and December 17th, 1925. (This list does not include titles of papers which have been read at an Ordinary Scientific Meeting, or which have appeared in the Journal.)

- "The mechanism of the formation of *o*- and *m*-hydroxybenzaldehydes from the nitration product of benzaldehyde." By H. H. HODGSON and H. G. BEARD.
- "The constitution of the normal monosaccharides. Part III. Rhamnose." By E. L. HIRST and A. K. MACBETH.
- "Resolution of *dl*-dicentrine." By R. D. HAWORTH, W. H. PERKIN, and J. RANKIN.
- "Synthetical experiments in the isoquinoline group. Part VI. A synthesis of derivatives of paraberine." By R. CAMPBELL, R. D. HAWORTH, and W. H. PERKIN.
- "The action of alkaline arsenites on some halogenated organic compounds." By I. E. BALABAN.
- "The equivalent conductivity of solutions of sodium hydroxide and the mobility of the hydroxyl ion." By H. R. RAIKES, A. F. YORKE, and F. K. EWART.
- "An investigation of the zirconium in Colorado pitchblende." By O. FREE.
- "Some products from the resins of *Xanthorrhoea*, *Hastilis*, *X. Arborea*, and *X. Reflexa*." By H. H. FINLAYSON.
- "The nitration of  $\beta$ -naphthoic acid and some new amino- and nitro-naphthoic acids." By H. A. HARRISON and F. A. ROYLE.
- "Preparation of *p*-bromophenylhydroxylamine by the emulsification process. A modification." By R. D. HAWORTH and A. LAPWORTH.
- "Optical activity and the polarity of substituent groups. Part III. Menthyl acetophenone-*o*-carboxylate." By H. G. RULE and J. SMITH.
- "The crystal structure of catechol." By W. A. CASPARI.
- "The chlorination and bromination of 4-aminodiphenyl." By H. A. SCARBOROUGH and W. A. WATERS.
- "Studies of dynamic isomerism. Part XXI. The velocity of mutarotation of glucose and of tetramethylglucose in aqueous alcohols." By E. M. RICHARDS and T. M. LOWBY.
- "Studies of dynamic isomerism. Part XXII. The velocity of mutarotation of glucose and of tetra-acetylglucose in aqueous acetone." By G. G. JONES and T. M. LOWBY.

- "Some unsymmetrically substituted dinitro and diamino derivatives in the stilbene and tolane series. Part I. The fission of hydrogen chloride from 3:4'-dinitrostilbene dichloride." By H. A. HARRISON and H. WOOD.
- "The mercuration of aromatic substances. Part II. Ortho-nitrotoluene." By S. COFFEY.
- "N-Alkylated amidines." By M. SEN and J. N. RAY.
- "The equilibrium between ethyl alcohol and the alkali and alkaline earth salts. Part I." By D. G. R. BONNELL and W. J. JONES.
- "The dissociation pressures of alcoholates. Part I." By D. G. R. BONNELL and W. J. JONES.
- "Ethyl hydrogen sulphate. Part II." By M. A. HAMID, K. SINGH, and H. B. DUNNICLIFF.
- "Heterogeneous equilibria between the sulphates and nitrates of sodium and potassium and their aqueous solutions. Part I. The ternary systems." By M. A. HAMID.
- "Heterogeneous equilibria between the sulphates and nitrates of sodium and potassium and their aqueous solutions. Part II. The quaternary system  $H_2O-Na_2SO_4-NaNO_3-K_2SO_4-KNO_3$ ." By M. A. HAMID.
- "A new reaction of certain diazosulphonates derived from  $\beta$ -naphthol-1-sulphonic acid. Part I. The preparation of phthalazine, phthalazone, and phthalimidine derivatives from 4'-nitrobenzene-2-naphthol-1-diazosulphonate." By F. M. ROWE, E. LEVIN, A. C. BURNS, J. S. H. DAVIES, and W. TEPPER.
- "Substituted dihydropentazines—a new series of cyclic nitrogen compounds." By F. D. CHATTAWAY and G. D. PARKES.
- "Dvi-manganese." By J. G. F. DRUCE and F. H. LORING.
- "Preparation, hydrolysis, and reduction of the fluoro-, chloro-, and bromo-benzyl bromides." By J. B. SHOESMITH and R. H. SLATER.
- "Absorption spectra of condensed nuclear hydrocarbons." By N. S. CAPPEE and J. K. MARSH.
- "The melting points of the normal saturated dibasic acids." By D. A. FAIRWEATHER.
- "Tautomerism in the thyroxin molecule." By C. S. HICKS.
- "The structure of the normal monosaccharides. Part IV. Glucose." By E. L. HIRST.
- "An investigation of the hydrated fluoride of zirconium and the preparation of a hydrofluozirconic acid." By E. B. R. PRIDEAUX and E. C. ROFER.
- "3:4- and 2:5-Dimethoxyphenylhydrazine." By W. H. PERKIN and L. RUBENSTEIN.

- "Condensations involving active methyl groups in heterocyclic bases." By J. E. HUMPHRIES.
- "The system ferrous oxide-phosphoric acid-water and some of its oxidation products." By S. R. CARTER and N. H. HARTSHORNE.
- "Absorption spectra and tautomerism. Part I. Keto-enol tautomerism." By R. A. MORTON and W. C. V. ROSNEY.
- "Absorption spectra and tautomerism. Part II." By R. A. MORTON and E. ROGERS.
- "Absorption spectra of mesityl oxide." By R. A. MORTON.
- "The decomposition of substituted carbamyl chlorides by hydroxy-compounds. Part II. The influence of the constitution of the hydroxy-compound." By T. W. PRICE.
- "Substitution in vicinal trisubstituted benzene derivatives. Part IV." By L. RUBENSTEIN.
- "The complex salts of  $\beta\beta'\beta''$ -triaminotriethylamine with nickel and palladium." By F. G. MANN and W. J. POPE.
- " $\gamma\gamma'\gamma''$ -Triaminotripropylamine and its complex compounds with nickel." By F. G. MANN and W. J. POPE.
- "Preparation and reduction of methyleneanthrone." By E. de B. BARNETT and M. A. MATTHEWS.

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TROTMAN, SAMUEL RUSSELL, and TROTMAN, EDWARD RUSSELL. The bleaching, dyeing, and chemical technology of textile fibres. London 1925. pp. xii + 610. ill. 30s. net. (*Recd.* 10/12/25.)

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